Detection of Environmental Contaminants Caused by the Oil Spill in the Gulf of Mexico by GC and HPLC

Sky Countryman, Ngoc Nguyen, Jeff Layne, Kory Kelly, and Zeshan Aqeel
Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

The recent oil spill in the Gulf of Mexico is undeniably the largest oil leak in U.S. history. This work provides SPE, GPC, GC-FID, GC/MS, and HPLC analytical methods for analyzing the most common contaminants that originated from the leak: Polycyclic Aromatic Hydrocarbons (PAHs), Petroleum Hydrocarbons (PHCs), and Volatile Organic Compounds (VOCs).

Introduction

The 2010 Gulf of Mexico oil spill is the largest accidental marine oil spill in the history of the petroleum industry. Though massive efforts have been made to stop and/or control the damage, negative environmental impact has already occurred. The extent of the damage is not yet known. Since the majority of the spilled oil is composed of the Louisiana Sweet Crude, this oil contains a variety of compounds such as aliphatic, aromatic, and alkylaromatic hydrocarbons.

In order to help understand the impact that the oil spill has caused, laboratories are looking for rapid and robust analytical procedures to characterize the hydrocarbon contaminants. This work provides SPE, GPC, GC-FID, GC/MS, and HPLC analytical methods for analyzing the most common contaminants that originated from the leak: Polycyclic Aromatic Hydrocarbons (PAHs), Petroleum Hydrocarbons (PHCs), and Volatile Organic Compounds (VOCs).

Prior to analysis, samples underwent a cleanup or a sample preparation procedure. In this work, GPC was used as the initial cleanup technique for removing high molecular weight impurities. An alternative cleanup procedure was done with a silica gel SPE tube, Strata® EPH. Compared to traditional analytical methods which only characterize hydrocarbon samples as a whole, the Strata EPH tube fractionates the sample into an aromatic and aliphatic portions. This allows for a better understanding of the sample's toxic potential.

Following GPC cleanup or SPE fractionation, the components were analyzed by GC-FID, GC/MS, or HPLC. GC was used to analyze total petroleum hydrocarbon content, PAHs, oil, and VOCs while HPLC was used to analyze PAHs.

Results and Discussion

In order to understand the impact of the Gulf Oil spill contamination, the oil must first be extracted from the matrix and subjected to various cleanup procedures to remove potential interferences. There are various procedures that can be used for this work, including Liquid-Liquid Extraction (LLE), Gel Permeation Chromatography (GPC), and Solid Phase Extraction (SPE).

Oil leakeage into the Gulf of Mexico has contaminated plants, animals, and the beach itself. Although shellfish are at particular risk of contamination, the analysis of PAHs and other hydrocarbons from shellfish can be challenging due to the lipid content in animal tissue. The National Oceanic and Atmospheric Administration (NOAA) Technical Memorandum NMFS-NWFSC-59 for extraction and cleanup of sediments and tissues identifies GPC as a cleanup technique for removing high-molecular weight impurities using the EnviroSep™-ABC 350 x 21.2 mm column.[1]

Figure 1 shows the calibration solution indicating the window that would be used to collect the more toxic PAHs. The EnviroSep-ABC material was specifically designed to be used for this type of cleanup methodology. The carefully controlled particle size and pore size distribution of this material ensure that it maximizes separation between the target PAH isomers and the high-molecular weight impurities.

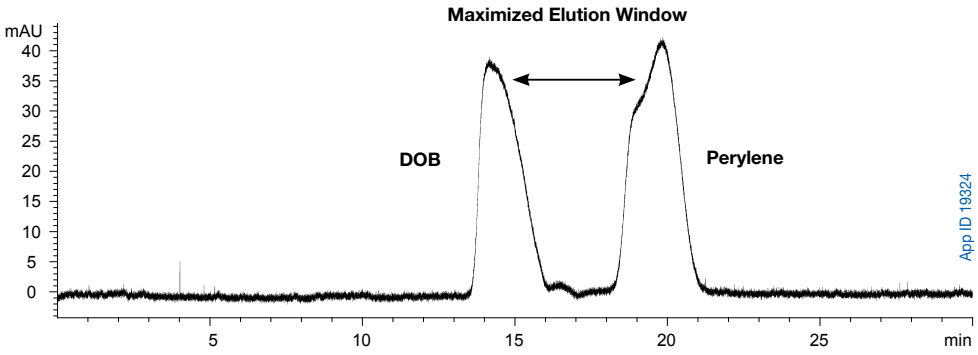
Traditional approaches to hydrocarbon testing provide a sum total of the material present in the sample but make no distinction between the different types of hydrocarbons. Newer methodologies utilize a silica gel SPE tube to fractionate the sample into aromatic and aliphatic portions so that a more accurate sample toxicity can be assigned **(Figure 2)**. The Strata EPH material was specially designed to overcome common problems with these methods, such as tube contamination and tube-to-tube flow consistency **(Figure 3)**. The Strata EPH material provides highly reproducible fractionation of petroleum samples **(Tables 1 and 2)**.

The EPA's sampling plan utilizes EPA Method 8015B for Total Petroleum Hydrocarbon (TPH) and EPA Method 8270 for semi-volatile contaminants including PAHs.[2] Total petroleum hydrocarbon analysis is a sum of what is considered the gasoline range organics (GRO) and the diesel or oil range organics (DRO or ORO).[3]

The lighter GRO fraction is commonly analyzed using purge and trap or other techniques that introduce only the volatile portion of the sample **(Figures 4 and 5)**. The Zebron ZB-1 and ZB-624 GC columns are able to improve retention for these volatile compounds, allowing for more accurate determination of the light hy-

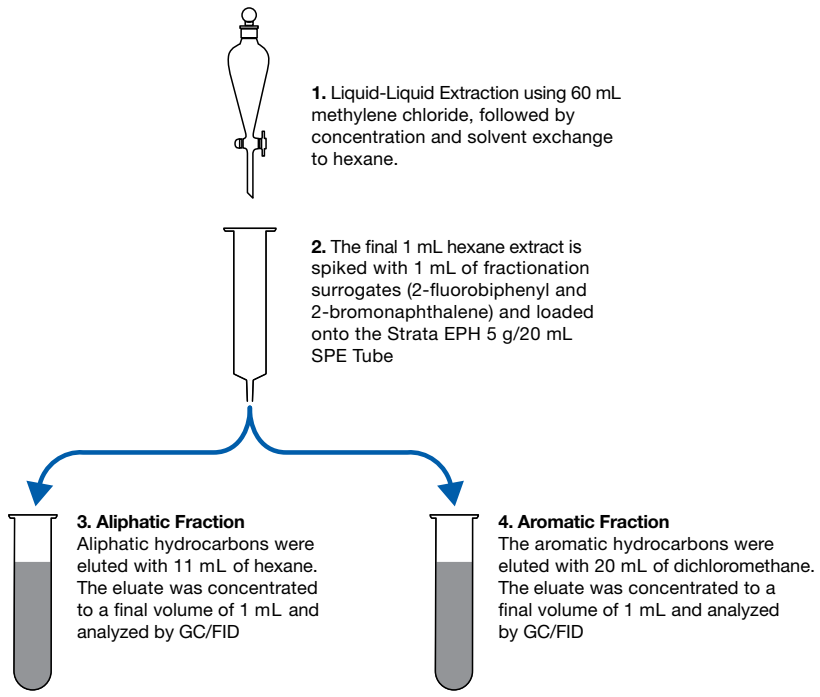
(text continued on p. 6)

Figure 1.
GPC Cleanup using EnviroSep™-ABC Following NOAA Technical Memorandum NMFS-NWFSC-5



Column: EnviroSep-ABC
Dimensions: 300 x 7.8 mm
Part No.: 00H-3035-K0
Mobile Phase: Methylene chloride
Flow Rate: 0.58 mL/min
Temperature: Ambient
Detector: UV @ 254 nm
Sample: 1. 4, 4´-Dibromooctafluorobiphenyl (DOB)
2. Perylene

Figure 2.
Extractable Petroleum Hydrocarbon (EPH) Fractionation Using Strata® EPH SPE Tubes



1. Liquid-Liquid Extraction using 60 mL methylene chloride, followed by concentration and solvent exchange to hexane.

2. The final 1 mL hexane extract is spiked with 1 mL of fractionation surrogates (2-fluorobiphenyl and 2-bromonaphthalene) and loaded onto the Strata EPH 5 g/20 mL SPE Tube

3. Aliphatic Fraction
Aliphatic hydrocarbons were eluted with 11 mL of hexane. The eluate was concentrated to a final volume of 1 mL and analyzed by GC/FID

4. Aromatic Fraction
The aromatic hydrocarbons were eluted with 20 mL of dichloromethane. The eluate was concentrated to a final volume of 1 mL and analyzed by GC/FID

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Figure 3.
Contamination Level of BHT from Strata® EPH and Conventional SPE Tubes

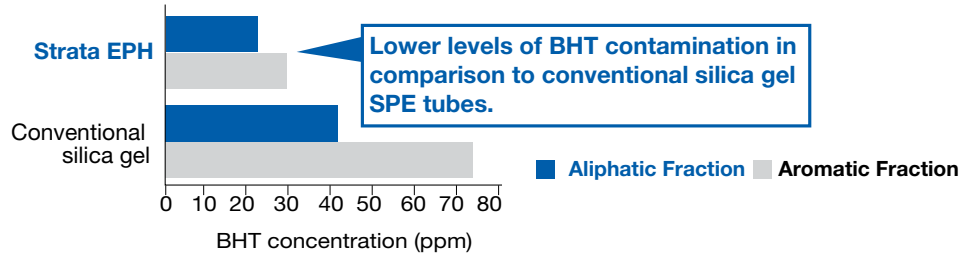
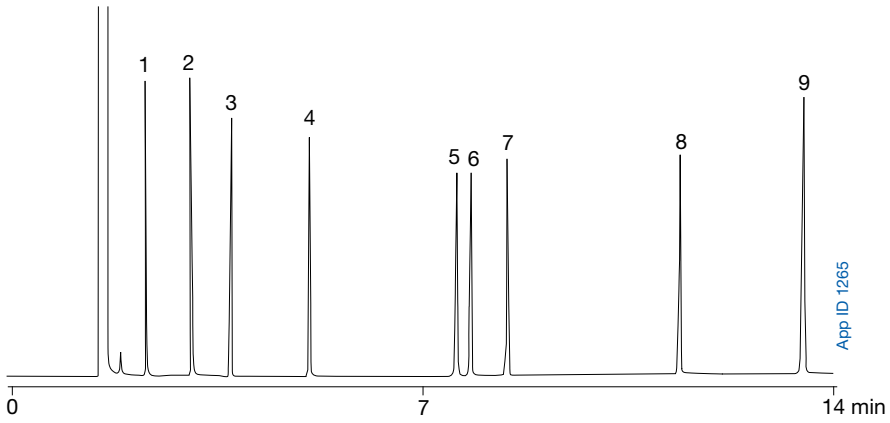


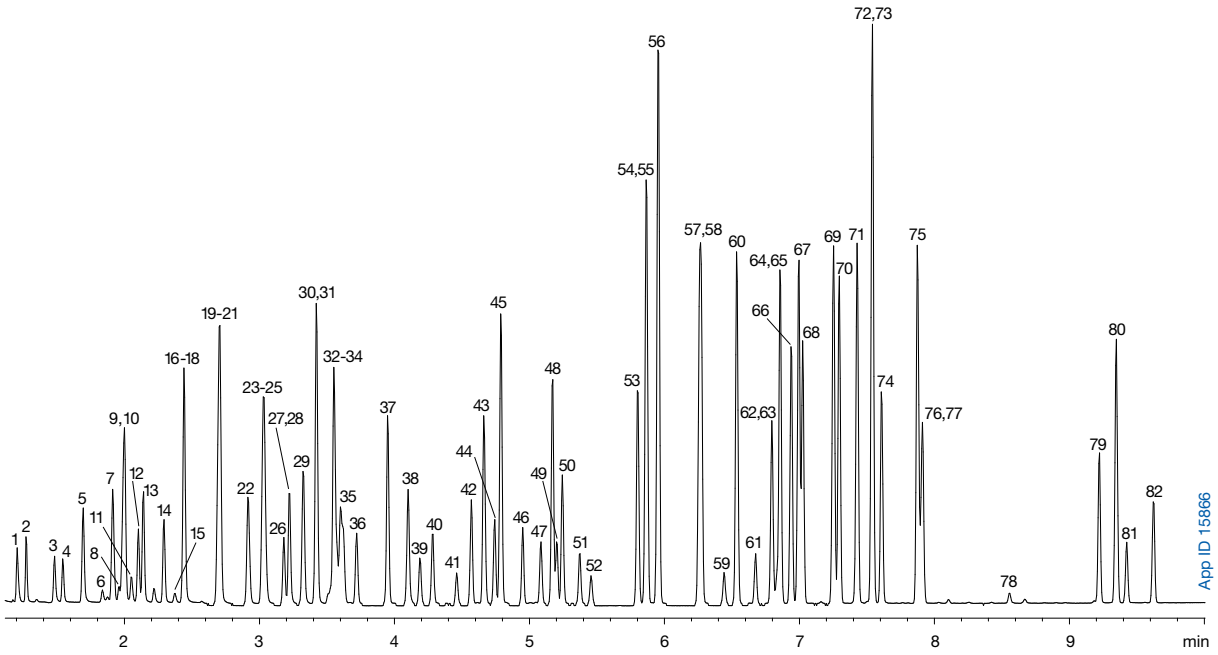
Figure 4.
Fast Gasoline Range Organic (GRO) Separation using Zebron™ ZB-1 GC Column



Column: Zebron ZB-1
Dimensions: 30 meter x 0.25 mm x 0.25 µm
Part No: 7HG-G001-11
Injection: Split 20:1 @ 250 °C, 1 µL
Carrier Gas: Helium @ 0.88 mL/min (constant flow)
Oven Program: 35 °C (2 min) to 110 °C @ 6 °C/min
Detector: FID @ 300 °C
Sample: 220 ppm GROs in Methanol

1. 3-Methylpentane
2. 2,2,4-Trimethylpentane
3. Benzene
4. Toluene
5. Ethylbenzene
6. m-Xylene
7. o-Xylene
8. 1,2,4-Trimethylbenzene
9. Naphthalene

Figure 5.
Fast Analysis of Volatile Organics (VOCs) from Water using Purge & Trap GC/MS



Column: Zebron™ ZB-624
Dimensions: 20 meter x 0.18 mm x 1.00 µm
Part No.: 7FD-G005-22
Injection: Purge and Trap
Carrier Gas: Helium (constant flow)
Oven Program: 35 °C to 210 °C
Detector: MSD; 35-275 amu
Sample:

1. Chloromethane
2. Vinyl chloride
3. Bromomethane
4. Chloroethane
5. Trichlorofluoromethane
6. Ethanol
7. Dichlorotrifluoroethane
8. Acrolein
9. Trichlorotrifluoroethane
10. 1, 1-Dichloroethene
11. Acetone
12. Methyl iodide
13. Carbon disulfide
14. Methylene chloride
15. t-Butanol
16. trans-1,2-Dichloroethane
17. Methyl-t-butyl ether
18. Acrylonitrile
19. 1, 1-Dichloroethane
20. Vinyl Acetate
21. Diisopropyl ether
22. Ethyl-t-butyl ether
23. 2, 2-Dichloropropane
24. cis-1, 2-Dichloroethene
25. 2-Butanone
26. Bromochloromethane
27. Chloroform
28. Tetrahydrofuran
29. 1, 1, 1-Trichloroethane
30. 1, 1-Dichloropropene
31. Carbon tetrachloride
32. 1, 2-Dichloroethane-d4
33. Benzene
34. 1, 2-Dichloroethane
35. t-Amyl methyl ether
36. Fluorobenzene
37. Trichloroethene
38. 1, 2-Dichloropropane
39. Dibromomethane
40. Bromodichloromethane
41. 2-Chloroethylvinyl ether
42. cis-1, 3-Dichloropropene
43. Methyl isobutyl ketone
44. Toluene-d8
45. Toluene
46. trans-1, 3-Dichloropropene
47. 1, 1, 2-Trichloroethane
48. Tetrachloroethene
49. 1, 3-Dichloropropane
50. 2-Hexanone
51. Dibromochloromethane
52. Ethylene dibromide
53. Chlorobenzene
54. 1, 1, 1, 2-Tetrachloroethane
55. Ethylbenzene
56. m,p-Xylene
57. o-Xylene
58. Styrene
59. Bromoform
60. Isopropylbenzene
61. 4-Bromofluorobenzene
62. 1, 1, 2, 2-Tetrachloroethane
63. Bromobenzene
64. 1, 2, 3-Trichloropropane
65. n-Propylbenzene
66. 2-Chlorotoluene
67. 1, 3, 5-Trimethylbenzene
68. 4-Chlorotoluene
69. tert-Butylbenzene
70. 1, 2, 4-Trimethylbenzene
71. sec-Butylbenzene
72. 1, 3-Dichlorobenzene
73. 4-Isopropyltoluene
74. 1, 4-Dichlorobenzene
75. n-Butylbenzene
76. 1, 2-Dichlorobenzene-d4
77. 1, 2-Dichlorobenzene
78. 1,2-Dibromo-3-chloropropane
79. 1, 2, 4-Trichlorobenzene
80. Hexachlorobutadiene
81. Naphthalene
82. 1, 2, 3-Trichlorobenzene

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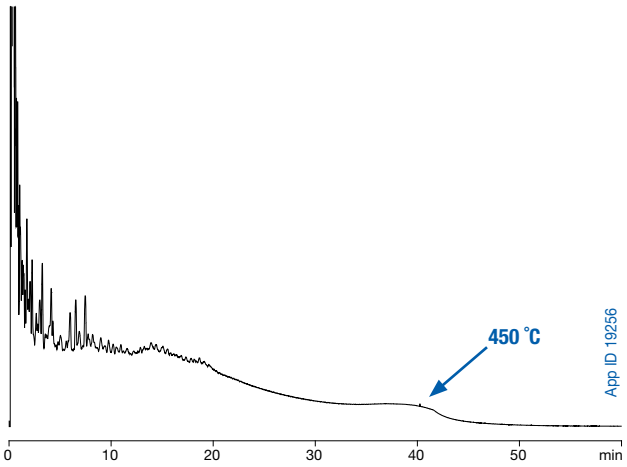
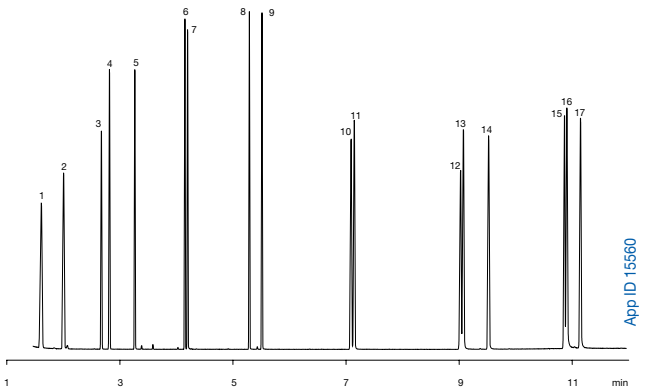
Figure 6.
Characterization of Crude Oil Sample using the Zebron™ ZB-1XT SimDist Metal GC Column



Column: Zebron ZB-1XT SimDist
Dimensions: 5 meter x 0.53 mm x 0.09 µm
Part No.: 7AK-G026-55
Injection: On-Column @ 38 °C, 1 µL
Carrier Gas: Helium @ 15 mL/min (constant flow)
Oven Program: 35 °C to 450 °C @ 10 °C/min for 20 min
Detector: FID @ 450 °C
Sample: Yeates Crude Oil

Note: Sample is 1 % in CS_2. Chromatogram is baseline subtracted.

Figure 7.
Fast Analysis of PAHs using Zebron ZB-5ms GC Column

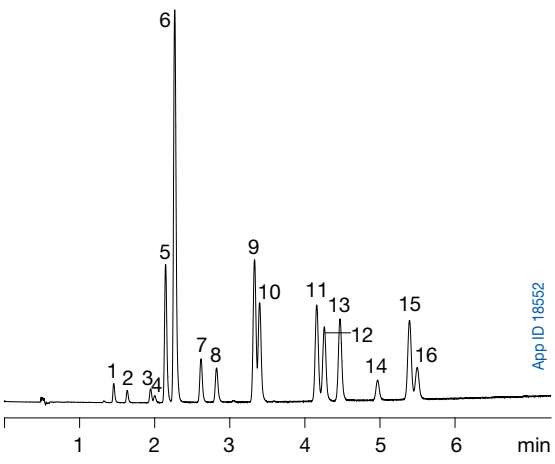


Column: Zebron ZB-5ms
Dimensions: 20 meter x 0.18 mm x 0.18 µm
Part No.: 7FD-G010-08
Injection: Split 15:1 @ 285 °C, 1 µL
Carrier Gas: Helium @ 1.2 mL/min (constant flow)
Oven Program: 130 °C for 0.5 min to 250 °C @ 25 °C/min to 270 °C @ 6 °C/min to 320 °C @ 25 °C/min for 4 min
Detector: MSD @ 180 °C; 40 - 400 amu
Sample:

1. Naphthalene
2. 2-Methylnaphthalene
3. Acenaphthalene
4. Acenaphthene
5. Fluorene
6. Phenanthrene
7. Anthracene
8. Fluoranthene
9. Pyrene
10. Benz[a]anthracene
11. Chrysene
12. Benzo[b]fluoranthene
13. Benzo[k]fluoranthene
14. Benzo[a]pyrene
15. Indeno[1,2,3-cd]pyrene
16. Dibenz[a,h]anthracene
17. Benzo[g,h,i]perylene

Note: Samples were 50 ppm in Dichloromethane

Figure 8.
HPLC Analysis of PAHs using Kinetex® Core-Shell C18



Column: Kinetex 2.6 µm C18
Dimensions: 100 x 4.6 mm
Part No.: 00D-4462-E0
Mobile Phase: A: Water
B. Acetonitrile
Gradient: (30:70) A/B to (0:100) A/B over 10 min
Flow Rate: 1.5 mL/min
Temperature: 30 °C
Detection: UV @ 254 nm
Sample:

1. Naphthalene
2. Acenaphthylene
3. Fluorene
4. Acenaphthene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Chrysene
10. Benz[a]anthracene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Dibenzo[a,h]anthracene
15. Indeno[1,2,3-cd]pyrene
16. Benzo[g,h,i]perylene

Table 1.
Results for the Aliphatic Fraction using Strata® EPH.

High Recoveries for the volatile C9-C12 hydrocarbons

Peak	Compound	% Recovery	% RSD (n = 3)
1	n-Nonane (C9)	88.4	2.3
2	n-Decane (C10)	91.9	2.3
3	n-Dodecane (C12)	92.8	2.2
4	n-Tetradecane (C14)	93.2	2.2
5	Butylhydroxytoluene (BHT)	—	—
6	n-Hexadecane (C16)	94.2	2.3
7	n-Octadecane (C18)	93.5	2.2
8	n-Nonadecane (C19)	91.1	1.9
9	n-Eicosane (C20)	92.8	1.9
10	5-α-Androstane (IS)	—	—
11	1-Chloro-Octadecane (Surr)	—	—
12	n-Docodane (C22)	92.9	1.8
13	n-Tetracosane (C24)	92.2	1.6
14	n-Hexacosane (C26)	92.4	1.6
15	n-Octacosane (C28)	93.4	1.5
16	n-Triacotane (C30)	95.9	1.4
17	n-Hexatriacontane (C36)	111.6	0.8

Table 2.
Results for the Aromatic Fraction using Strata EPH.

Low % RSD from tube to tube ensures reproducible fractionation

Peak	Compound	% Recovery	% RSD (n = 3)
1	Naphthalene	67.2	2.2
2	2-Methylnaphthalene	72.1	1.7
3	2-Fluorobiphenyl (Frac Surr)		1.0
4	Acenaphthalene	72.9	1.3
5	2-Bromonaphthalene (Frac Surr)		
6	Acenaphthene	76.2	1.3
7	Phthalate	97.9	
8	Fluorene	92.8	2.2
9	Phenanthrene	84.0	2.7
10	Anthracene	84.3	2.2
11	o-Terphenyl (Surr)		
12	5-α-Androstane		
13	Fluoranthene	84.1	2.2
14	1-Chloro-Octadecane (Surr-Aliphatic)		
15	Pyrene	88.3	2.2
16	Benz[a]anthracene	87.4	2.0
17	Chrysene	97.0	2.0
18	Benzo[b]fluoranthene	90.6	2.4
19	Benzo[k]fluoranthene	91.9	1.7
20	Benzo[a]pyrene	91.4	1.7
21	Indeno[1,2,3-cd]pryene	94.8	1.1
22	Dibenz[a,h]anthracene	92.7	1.2
23	Benzo[g,h,i]perylene	90.5	1.1

drocarbons present in the sample. This is important because the lighter hydrocarbons are the ones that populations in the region are likely to be exposed to from inhalation.

The heavier DRO or ORO portion of the sample can include hydrocarbons from C10 to C44 or more. Based on the high asphaltene content in the early samples received by Ed Overton's group at Louisiana State University, the gulf oil crude may contain very heavy hydrocarbons that cannot be eluted using traditional polyimide-coated GC columns. Such cases require the use of specialized metal GC columns, such as the Zebron™ ZB-1XT SimDist columns, which can be used to characterize hydrocarbon samples containing species higher than C120 **(Figure 6)**.

PAHs are a particularly toxic class of compounds found in petroleum products and pose a significant health risk. The EPA gives two primary techniques for the analysis of PAH in solid materials, GC/MS and HPLC. The primary method proposed for the cleanup effort is EPA Method 8270, which uses GC/MS. The Zebron ZB-5ms GC column improves resolution of isomers, such as Benzo[b] and Benzo[k]fluoranthene, allowing for the analysis time to be shortened to accommodate higher sample throughput **(Figure 7)**.

The analysis of PAHs can also be done using HPLC, following EPA Method 8310 guidelines. There have been significant advances in particle technology and HPLC systems in the past several years that allow many older methods to be dramatically improved. One such technology is the Kinetex® core-shell particle, which provides ultra-high efficiency separations on standard HPLC instruments. Using these columns, the separation of the standard 16 PAH compounds can be done in less than six minutes **(Figure 8)**.

Conclusion

Due to the magnitude of the Gulf Oil spill, the cleanup will be on-going for many years and there is not one specific technique that can be applied to all samples. We have presented here just a few of the solutions that are available. Additional solutions are being developed every day for other chemicals, such as dispersants, used in the cleanup process. For more information about these and other solutions available, please visit: www.phenomenex.com.

References

1. Extraction, Cleanup, and Gas Chromatography/Mass Spectrometry Analysis of Sediments and Tissues for Organic Contaminants, U.S. DEPARTMENT OF COMMERCE National Oceanic and Atmospheric Administration, March 2004.
2. QUALITY ASSURANCE SAMPLING PLAN FOR BRITISH PETROLEUM OIL SPILL, U.S. Environmental Protection Agency, May 2010.
3. EPA Method 8015B NON-HALOGENATED ORGANICS USING GC/FID, Environmental Protection Agency, Revision 2, 1996.

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Ordering Information

EnviroSep™-ABC GPC Columns

Phenomenex Part No.	ABC Lab Part No.	Description	Size (mm)
03R-3035-P0	417-250	Preparative Guard	60 x 21.2
00W-3035-P0	417-150	Preparative Column	350 x 21.2
03B-3035-K0	417-200	Analytical Guard	50 x 7.8
00H-3035-K0	417-151	Analytical Column	300 x 7.8

Kinetex® 2.6 µm Analytical HPLC Columns (mm)

	30 x 4.6	50 x 4.6	75 x 4.6	100 x 4.6	150 x 4.6	SecurityGuard™ Ultra Cartridges‡ /3pk	KrudKatcher™ Ultra In-Line Filter* /3pk
XB-C18	—	00B-4496-E0	00C-4496-E0	00D-4496-E0	00F-4496-E0	AJ0-8768	AF0-8497
C18	00A-4462-E0	00B-4462-E0	00C-4462-E0	00D-4462-E0	00F-4462-E0	AJ0-8768	AF0-8497
C8	—	00B-4497-E0	00C-4497-E0	00D-4497-E0	00F-4497-E0	AJ0-8770	AF0-8497
PFP	00A-4477-E0	00B-4477-E0	00C-4477-E0	00D-4477-E0	00F-4477-E0	AJ0-8773	AF0-8497
HILIC	—	00B-4461-E0	00C-4461-E0	00D-4461-E0	00F-4461-E0	AJ0-8772	AF0-8497

for 4.6 mm ID

‡SecurityGuard Ultra cartridges require holder, Part No.: AJ0-9000. Check for availability in your country.
*KrudKatcher Ultra requires 5/16 in. wrench. Wrench not provided.

Strata® EPH Solid Phase Extraction

Format	Sorbent Mass	Part Number	Unit
Tube			
	500 mg	8B-S031-HBJ	3 mL (50/box)
Giga™ Tube			
	5 g	8B-S031-LEG	20 mL (20/box)
Teflon® Giga Tube			
	5 g	8B-S031-LEG-T	20 mL (20/box)

Zebron™ ZB-624 GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
20-Meter			
0.18	1.00	-20 to 260	7FD-G005-22
30-Meter			
0.25	1.40	-20 to 260	7HG-G005-27
0.32	1.80	-20 to 260	7HM-G005-31
0.53	3.00	-20 to 260	7HK-G005-36
60-Meter			
0.25	1.40	-20 to 260	7KG-G005-27
0.32	1.80	-20 to 260	7KM-G005-31
0.53	3.00	-20 to 260	7KK-G005-36

Zebron ZB-5ms GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
20-Meter			
0.18	0.18	-60 to 325/350	7FG-G010-08
0.18	0.32	-60 to 325/350	7FG-G010-51
0.18	0.36	-60 to 325/350	7FG-G010-53
30-Meter			
0.25	0.25	-60 to 325/350	7HG-G010-11

Zebron ZB-1XT SimDist Metal GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
5-Meter			
0.53	0.09	-60 to 450	7AK-G026-55
0.53	0.15	-60 to 450	7AK-G026-05
10-Meter			
0.53	0.15	-60 to 450	7CK-G026-05
0.53	2.65	-60 to 400	7CK-G026-35

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G010-11-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

guarantee

If Phenomenex products in this technical note do not provide at least an equivalent separation as compared to other products of the same phase and comparable dimensions, return the product with comparative data within 45 days for a FULL REFUND.

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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

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