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

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Introduction

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.

Abstract

The April 2010 oil spill in the Gulf of Mexico is undeniably the largest oil leak in U.S. history. The objective of this work was to provide analytical methods for analyzing the most common contaminants. Several rapid cleanup procedures utilizing SPE or GPC followed by analysis with GC-FID, GC/MS or HPLC were developed for detecting Polycyclic Aromatic Hydrocarbons (PAHs) and other Petroleum Hydrocarbons.

Total petroleum content in aqueous samples was determined by GC and classified by boiling point range: gasoline range (GRO), diesel range (DRO), or oil range organics (ORO).
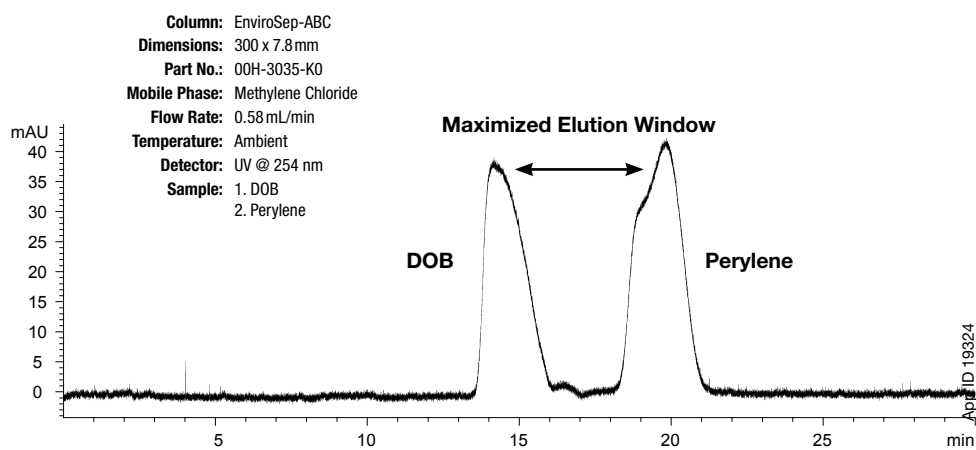
The nature of some of the early samples collected suggested that it was composed of extremely high molecular weight materials with boiling ranges in the ORO. These samples require the use of specialized metal GC columns that are capable of withstanding temperatures above 430 °C. Methodologies are presented to characterize hydrocarbon samples that contain species higher than C120.

Traditional approaches to hydrocarbon testing provide a sum of the hydrocarbon material present in the sample but make no distinction between the types of hydrocarbons. While these methods give a general understanding of the sample, they do not accurately describe its toxic potential. To give a more accurate assessment of sample toxicity, samples are fractionated using a silica gel SPE cartridge into an aromatic and an aliphatic portion. The fractions are then run separately by GC-FID and the level of specific compounds that are known to be toxic can be measured. An alternative procedure of extracting PAH isomers from water using solid phase extraction (SPE) followed by analysis by GC/MS is also demonstrated.

Figure 1. GPC Cleanup Using EnviroSep™-ABC Following NOAA Technical Memorandum NMFS-NWFSC-59

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. DOB
2. Perylene

Maximized Elution Window

DOB

Perylene

App ID 19324

Results and Discussion

Oil leakage 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 mm 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 the separation between the target PAH isomers and the high-molecular weight impurities is maximized.

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 cartridge 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 provides highly reproducible fractionation of petroleum samples (**Tables 1 & 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 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 3**).

PAHs are a particularly toxic class of compounds found in petroleum products that 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 4**).

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 6 minutes (**Figure 5**).

Figure 2. Extractable Petroleum Hydrocarbon (EPH) Fractionation Using Strata EPH
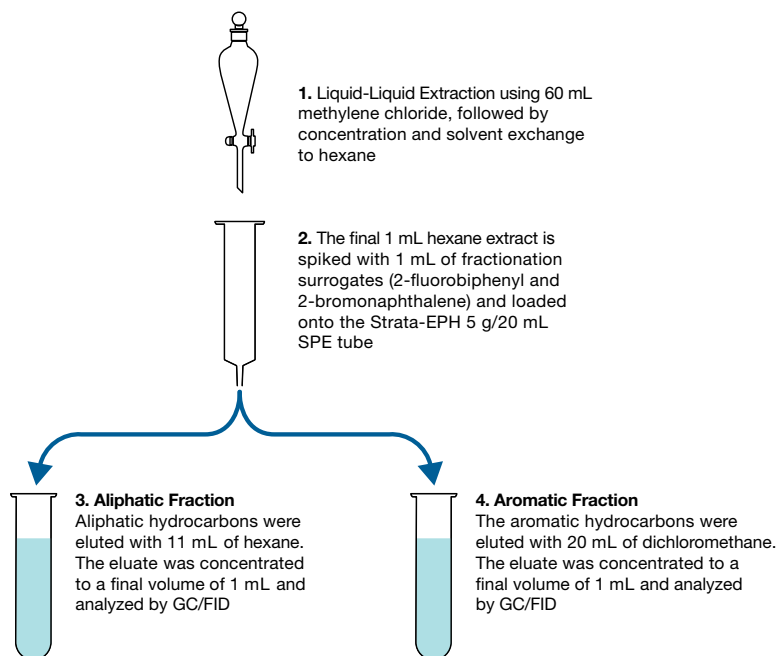
1. Liquid-Liquid Extraction using 60 mL methylene chloride, followed by concentration and solvent exchange to hexane

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

Table 1. Results for the Aliphatic Fraction Using Strata-EPH

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

← High recoveries for the volatile C9-C12 hydrocarbons

Table 2. Results for the Aromatic Fraction Using Strata-EPH

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	Phanthrene	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

← Low % RSD from tube to tube ensures reproducible fractionation

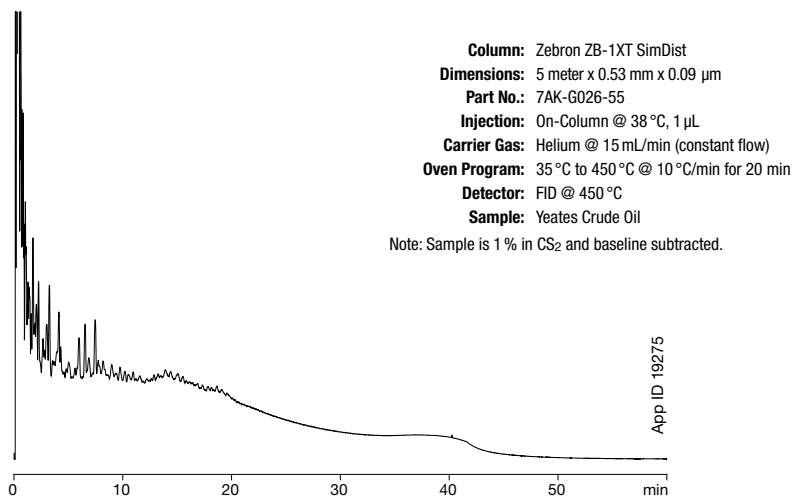**Figure 3. Characterization of Crude Oil Sample Using the Zebron ZB-1XT SimDist GC Column**

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 and baseline subtracted.

App ID 19275

Figure 4. Fast GC Analysis of PAH Isomers Using Zebron ZB-5ms

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; 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

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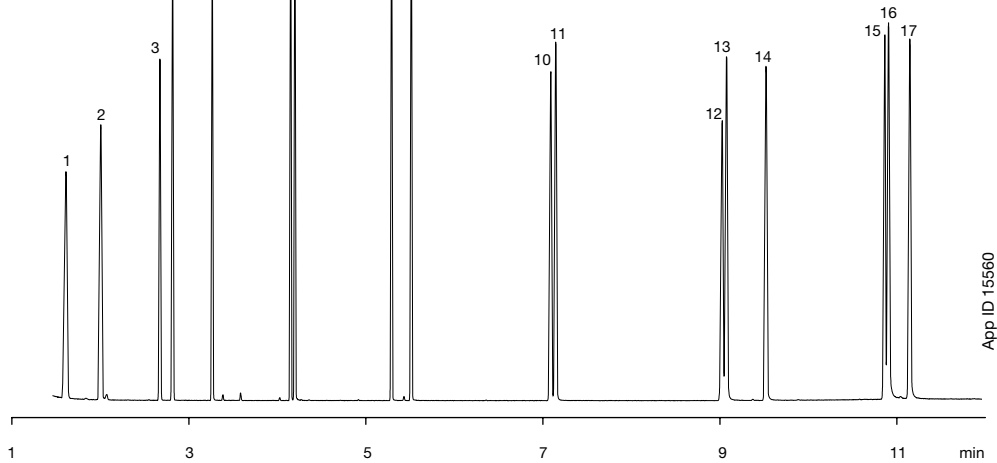
Figure 5. HPLC Analysis of PAHs Using Kinetex Core-Shell C18
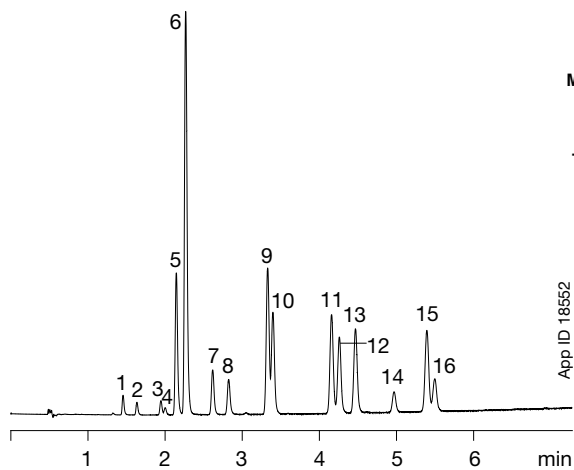
Column:	Kinetex 2.6 µm C18
Dimensions:	100 x 4.6 mm
Part No.:	00D-4462-E0
Mobile Phase:	A: Water
	B. Acetonitrile
Gradient:	(30:70) A/B to (0:100) A/B over 10 min
Flow Rate:	1.5 mL/min
Temperature:	30 °C
Detection:	UV @ 254 nm

Sample:

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

App ID 18552

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 NONHALOGENATED ORGANICS USING GC/FID, Environmental Protection Agency, Revision 2, 1996