Fractionation of Aliphatic and Aromatic Hydrocarbons in Petroleum Extracts

UCT Part Numbers

XRSIHT15M25
ENVIRO-CLEAN® EPH Fractionation 5000mg/25mL (Gravity Flow) Capped at both ends to ensure silica integrity

VMF016GL
16 position glass block manifold

VMF02116
Pack of 16 stopcocks

VMF02125
12 position large volume collection rack

GCLGN4MM-5
GC liner, 4mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm

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Summary:

The composition of petroleum is a complex mixture of hundreds of different hydrocarbon compounds. The resultant makeup of hydrocarbons released into the environment is variable and dependent on the conditions to which it is subsequently exposed. While in the environment, petroleum composition is influenced by a number of factors including volatilization, leaching, and/or biological degradation. These environmental effects yield a mixture whose toxicological properties can be vastly different than the parent product. Based on the known toxicological properties of petroleum products, aromatic compounds are more toxic than aliphatic compounds, and the toxicity of aliphatic compounds is dependent upon their molecular weights with low molecular weight compounds showing relatively higher toxicity.

The fractionation of the total extractable petroleum hydrocarbons (EPH) is necessary to determine the concentration of the aliphatic versus aromatic compounds. The Massachusetts Department of Environmental Protection (MADEP) utilizes the unbonded silica gel solid phase extraction (SPE) cartridges to fractionate the C9-C18 aliphatic hydrocarbons (n-nonane to n-octadecane), C19-C36 aliphatic hydrocarbons (n-nonadecane to hexatriacontane), and the C11-C22 aromatic hydrocarbons (naphthalene to benzo(ghi)perylene) [1]. The EPH are extracted into methylene chloride (DCM) from water, soil, or sediment samples using different extraction methods described in the MADEP EPH method, then concentrated and exchanged into 1 mL n-hexane before fractionating on the silica gel SPE cartridges. The retained EPH are later eluted into 2 fractions using organic solvents with different polarities, n-hexane for elution of the aliphatic fraction, while DCM for the aromatic fraction.

Precautions:

Silica gel is hygroscopic and can be deactivated by moisture in the air, resulting in poor performances, such as inconsistent results, low recoveries, and naphthalene/2-methylnaphthalene breakthrough into the aliphatic fraction. Precautions should be taken when storing and using the silica gel cartridges to prevent deactivation of the silica gel sorbent. Unopened packages should be stored in a dry and clean environment, while the opened ones should be resealed and stored in a well maintained desiccator until the next use.

Fractionation Procedure:

1. **Cartridge Conditioning**
   a) Remove the caps from both ends of the silica gel SPE cartridges (**XRSIHT15M25**), and attach the SPE cartridges to the stopcocks (**VMF02116**) on a 16-position glass block manifold (**VMF016GL**). Add 10 mL of n-hexane IMMEDIATELY into the cartridges to prevent silica gel from adsorbing the ambient moisture.
   b) Allow hexane pass through the SPE cartridges at a drop-wise fashion by GRAVITY, no vacuum should be applied during the whole procedure.
   c) Add 2 more aliquots of 10 mL hexane. Close the stopcock to stop the flow once the hexane level reaches the top frit. Do not allow the top frit or the silica gel sorbent go dry.

2. **Sample Loading**
   a) Add 1 mL EPH standard prepared in hexane or sample extract (exchanged into 1 mL hexane) to the SPE cartridges, 0.5 mL hexane rinse can be used to ensure quantitative transfer.
   b) Let samples pass by gravity until the level reaches the top frit, then close the stopcock.

3. **Elution**
   a) Insert the 12-position collection rack (**VMF02125**) with 40-mL VOA glass vials into the manifold.
   b) Elute the aliphatic fraction with 20* mL of n-hexane (2 x 10 mL) by gravity, collect and label the eluates as “aliphatic”.
   c) Remove the vials with aliphatic fractions from the collection rack, and insert new VOA vials to collect the aromatic fractions.
   d) Elute the aromatic fraction with 20 mL of DCM (2 x 10 mL) by gravity, collect and label the eluates as “aromatic”.

5. **Concentration**
   a) Add internal standard (IS), and concentrate the eluates to 1 mL or a higher volume if the desired detection limits can be achieved. In this study the eluates are evaporated to 10 mL using TurboVap under a gentle stream of nitrogen at 40 ºC.
   b) Transfer 1 mL each to 2-mL autosampler vials, and analyze the 2 fractions separately by GC/MS.

**: The volume of n-hexane should be optimized so that only the aliphatic hydrocarbons are eluted without breakthrough of the aromatic hydrocarbons into the aliphatic fraction (the naphthalene and 2-methyl naphthalene breakthrough should be <5%). The optimum hexane volume may vary from lab to lab, depending on the moisture content in the lab environment.*

GC/MS Method:

Parameters	Conditions
GC/MS	Agilent 6890N GC coupled to 5975C MSD
Injection	1 µL splitless injection at 250 ºC
GC liner (**GCLGN4MM-5**)	4 mm splitless gooseneck liner with deactivated glass wool
GC column	Restek Rxi®-5sil MS 30m x 0.25mm, 0.25µm with 10m integrated guard column
Carrier gas	Ultra-high purity Helium at a constant flow of 1.5 mL/min
Oven temp. program	Initial temperature at 40 ºC, hold for 3 min; ramp at 15 ºC/min to 240 ºC; ramp at 6 ºC/min to 310 ºC; and hold for 5 min
Temperatures	Transfer line 280 ºC; Ion source 250 ºC; Quadrupole 150 ºC
Full scan range	40 - 510 amu

Results:

Breakthrough of Aromatic Hydrocarbons into the Aliphatic Fraction

Aromatic Hydrocarbons	Breakthrough%
Naphthalene	0.1
2-Methylnaphthalene	0.0

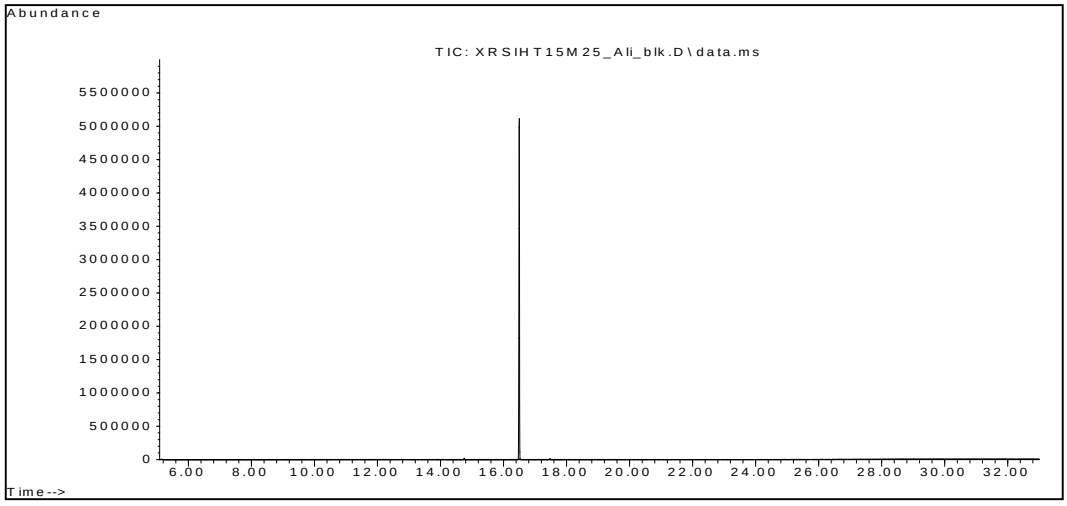
Demonstration of Fractionation Efficiency - Aliphatic Fraction

Aliphatic Hydrocarbons	Recovery%	RSD% (n=4)
Chloro-octadecane Surr	89.7	2.2
C9	87.8	1.6
C10	89.9	1.9
C12	90.9	2.5
C14	92.5	2.3
C16	92.7	2.1
C18	92.5	2.4
C19	109.2	2.4
C20	92.6	2.1
C22	93.1	2.1
C24	92.2	2.5
C26	92.1	2.3
C28	97.6	2.4
C30	90.3	1.7
C36	89.8	2.9
Aliphatic C9 - C18	**91.0**	**2.1**
Aliphatic C19 -C36	**94.6**	**2.3**

Demonstration of Fractionation Efficiency - Aromatic Fraction

Aromatic Hydrocarbons	Recovery%	RSD% (n=4)
o-Terphenyl Surr	93.8	3.3
Naphthalene	92.4	2.9
2-Methylnaphthalene	91.6	3.0
Acenaphthylene	91.9	3.1
Acenaphthene	92.1	2.5
Fluorene	91.2	2.6
Phenanthrene	91.3	2.8
Anthracene	91.2	2.7
Fluoranthene	91.1	2.9
Pyrene	91.0	3.1
Benz[a]anthracene	90.4	2.7
Chrysene	91.7	3.0
Benzo[b]fluoranthene	91.7	2.9
Benzo[k]fluoranthene	88.5	2.8
Benzo[a]pyrene	88.8	2.7
Indeno[1,2,3-cd]pyrene	88.8	2.8
Dibenz[a,h]anthracene	89.0	3.7
Benzo[ghi]perylene	89.1	2.5
Aromatic C11 - C22	**90.7**	**2.8**

Chromatograms



(a) Aliphatic fraction of a blank sample fractionated using silica gel cartridge

(IS: 5-alpha-androstane at 16.51 min)

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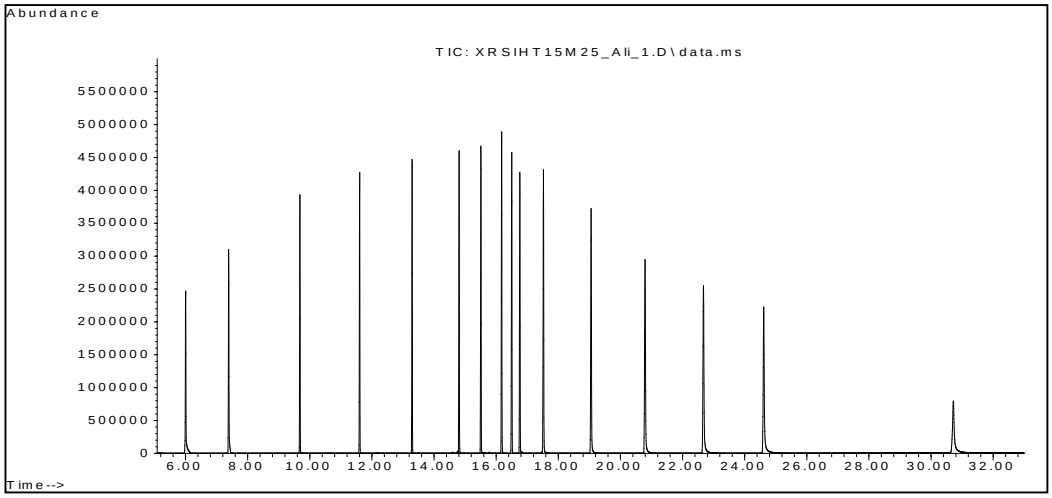
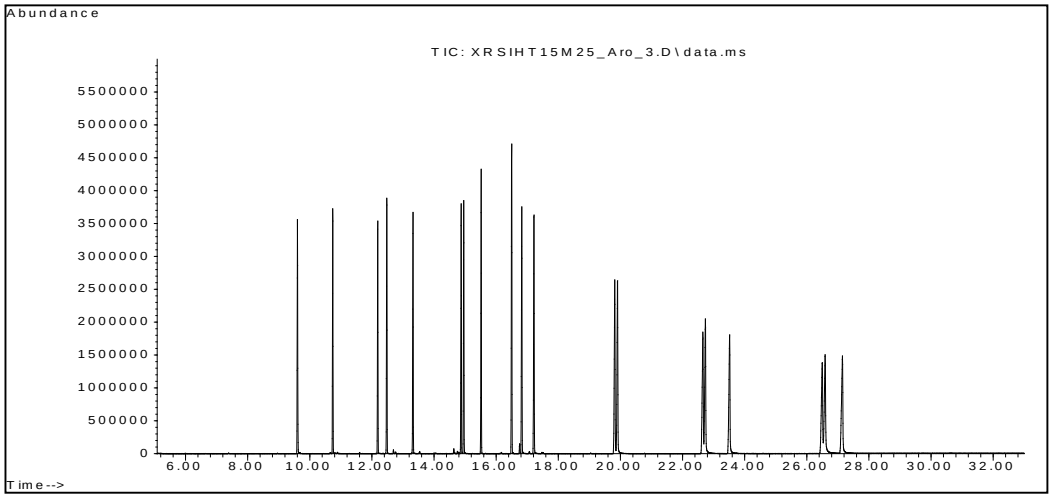


(b) Aliphatic fraction of a fractionation check sample at 200 µg/L



(c) Aromatic fraction of a fractionation check sample at 200 µg/L

Conclusions:

Excellent analytical performance has been obtained using UCT's EPH silica gel SPE cartridges (heat treated, large particle size) for the fractionation of aliphatic and aromatic hydrocarbons. Recoveries were ranged from 90.7 to 94.6% for 3 EPH fractions, aliphatic C9 – C18, C19 to 36, and aromatic C11 – C22, with relative standard deviations (RSD%) < 3%, which well passed the QC requirements set by the MADEP EPH method: 40 - 140% in recovery and RSD% < 25%. The naphthalene and 2-methyl naphthalene breakthrough was < 1%, also met the required <5% breakthrough of the aromatics into the aliphatic fraction, offering testing labs a reliable silica gel product for the cleanup and fractionation of EPH in environmental samples.

References:

[1] http://www.mass.gov/eea/docs/dep/cleanup/laws/eph0504.pdf

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