Improved Hydrocarbon Fractionation Using a Novel Silver-Phase SPE Sorbent

UCT Part Numbers

ECFUSAG156
ENVIRO-CLEAN® Fusion®AG+
500 mg, 6 mL cartridge

Or

ECFUSAG1M6
ENVIRO-CLEAN® Fusion®AG+
1 g, 6 mL cartridge

Or

ECFUSAG2M6
ENVIRO-CLEAN® Fusion®AG+
2 g, 6 mL cartridge

VMF024GL
24 position glass block manifold

ENVIRO

Summary:

Water, sediment, and soil are routinely analyzed in the US for extractable petroleum hydrocarbon (EPH) to assess the risk posed by petroleum products in the environment. To obtain an accurate profile of the total EPH, the aliphatic and aromatic hydrocarbons are fractionated and analyzed separately to help identify their health risks. Fractionation of aliphatic and aromatic hydrocarbons is typically carried out according to the Massachusetts Department of Environmental Protection (MADEP) or New Jersey Department of Environmental Protection (NJDEP) protocols using solid-phase extraction (SPE) with heat-treated silica gel [1,2]. One of the biggest problems encountered with this approach is the deactivation of the silica gel due to its hygroscopic nature, which can lead to inconsistent results, low recoveries, and breakthrough of the aromatic fraction into the aliphatic fraction (or vice versa). Furthermore, the volume of n-hexane has to be optimized for each batch of silica cartridges so that only the aliphatic hydrocarbons are eluted without breakthrough of the aromatic hydrocarbons (e.g. naphthalene and 2-methyl naphthalene). This can be a time-consuming and tedious process that is far from ideal for high-throughput testing labs.

This application note outlines a new specialized SPE sorbent designed to help overcome the challenges associated with traditional silica gel fractionation. The new EPH fractionation sorbent consists of silver ions functionalized onto a solid support. Aromatic hydrocarbons are selectively retained on the sorbent by forming a charge-transfer complex with the silver ions. This ensures high capacity for the aromatic hydrocarbons and no breakthrough into the aliphatic fraction. Consistent lot-to-lot reproducibility without the need to optimize the elution solvent for each batch of cartridges are two of biggest advantages of this new sorbent. In addition, the fractionation protocol is easier, faster, uses less solvent than silica cartridges, while the use of acetone instead of dichloromethane as the elution solvent for the aromatic fraction is significantly more environmentally friendly.

Product Highlights:

Unique Sorbent – silver ions functionalized onto a solid support.

Highly Selective – aromatic hydrocarbons form a charge-transfer complex with the silver ions.

No Breakthrough – of aromatic fraction into the aliphatic fraction, including the more polar naphthalene and 2-methylnaphthalene.

Complete Separation – of aliphatic and aromatic fractions.

High Capacity – excellent capacity for the aromatic hydrocarbons. Much higher capacity relative to heat treated silica gel (25 mg/g).

Excellent Lot-To-Lot Reproducibility – excellent reproducibility across different batches of sorbent.

Simplified Procedure – optimized protocol is easier, faster, and uses less solvent than silica cartridges. In addition, there is no need to optimize the elution solvent for each batch of cartridges.

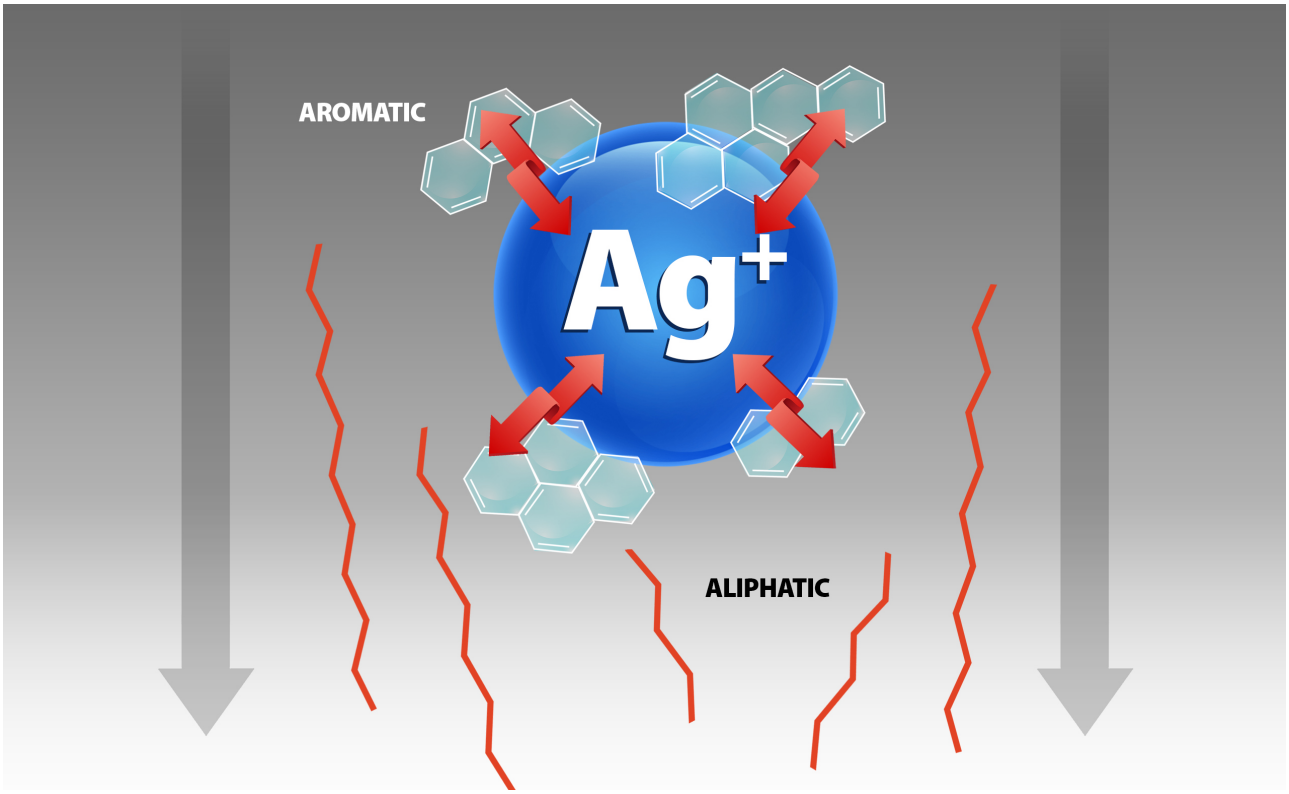
Improved Stability – sorbent is not deactivated by moisture.

Excellent Analytical Performance – recoveries primarily in the 80 to 110% range with relative standard deviation (RSD) less than 10%.

More Environmentally Friendly – the use acetone instead of dichloromethane as the elution solvent for the aromatic fraction is more environmentally friendly. Uses less solvent overall compared to fractionation procedure with heat treated silica.

Three Formats Available – 500mg, 1g or 2g for higher capacity.

Amenable to Automation – improves day-to-day reproducibility and increased sample throughput.



ENVIRO

Precautions:

- Do not remove SPE cartridges from packaging until ready for use.
- Protect cartridges from direct UV light and store columns in their protective packaging until use. Silver ions on the sorbent are oxidation labile. Store unused cartridges in their packaging until use. Such storage will avoid possibility of oxidation.

Sample Preparation:

- Water samples should be prepared in accordance to USEPA Method 3510 (separatory funnel liquid-liquid extraction).
- Soil samples should be prepared in accordance to USEPA Methods 3540 (Soxhlet extraction) or 3546 (microwave extraction).

SPE Procedure:

The following SPE procedure should be performed under gravity (no vacuum should be applied at any point). There is no need to close the stopcocks in-between each step as long as the cartridges are not allowed to sit idle for a significant period of time (>5 minutes).

The procedure below is for a 1 g cartridge size. For a 500 mg cartridge size change the conditioning and elution volumes to 2 mL. For the 2 g cartridge size change the conditioning and elution volumes to 6 mL. The remainder of the procedure stays the same.

1. Cartridge Conditioning

a) 1 × 4 mL acetone – let solvent pass by gravity until dripping ceases (send to waste).
a) 1 × 4 mL *n*-hexane – let solvent pass by gravity until dripping ceases (send to waste).

2. Sample Loading & Fractionation

a) Insert a collection rack containing glass collection tubes into the SPE manifold. Label these collection tubes as “aliphatic”.
b) Add the sample extract (exchanged into 1 mL *n*-hexane) containing surrogates and fractionation surrogates to the SPE cartridge.
    - Alternatively, add 1 mL of the EPH standard prepared in *n*-hexane to the SPE cartridge.
c) Let samples pass by gravity until dripping ceases.
    - An additional 0.5-1 mL hexane rinse of the sample container can be used to ensure quantitative transfer of the sample to the SPE cartridge.
d) Elute the aliphatic fraction with 4 mL of *n*-hexane.
e) Remove the tubes with the aliphatic fractions from the collection rack, and insert new glass collection tubes to collect the aromatic fraction. Label these collection tubes as “aromatic”.
f) Elute the aromatic fraction with 4 mL of acetone.

3. Concentration

1. Add internal standard (IS) and concentrate the samples to 1 mL. Be careful not to concentrate below 1 mL.
2. Transfer samples to autosampler vials and analyze the two fractions separately.

- Alternatively, if the desired detection limits can be achieved without concentrating the extract, simply add the internal standard (IS), vortex, and transfer an aliquot to an autosampler vial for analysis.

ENVIRO

Compounds Evaluated:

	Aliphatics	Aromatics
1	1-Chlorooctadecane (surrogate)	o-Terphenyl (surrogate)
2	(C9) n-Nonane	2-Bromonaphthalene (fractionation surrogate)
3	(C10) n-Decane	2-Fluorobiphenyl (fractionation surrogate)
4	(C12) n-Dodecane	1,2,3-Trimethylbenzene
5	(C14) n-Tetradecane	2-Methylnaphthalene
6	(C16) n-Hexadecane	Acenaphthene
7	(C18) n-Octadecane	Acenaphthylene
8	(C19) n-Nonadecane	Anthracene
9	(C20) n-Eicosan	Benzo[a]anthracene
10	(C21) n-Heneicosane	Benzo[a]pyrene
11	(C22) n-Docosane	Benzo[b]fluoranthene
12	(C24) n-Tetracosane	Benzo[ghi]perylene
13	(C26) n-Hexacosane	Benzo[k]fluoranthene
14	(C28) n-Octacosane	Chrysene
15	(C30) n-Triacontane	Dibenz[a,h]anthracene
16	(C32) n-Dotriacontane	Fluoranthene
17	(C34) n-Tetratriacontane	Fluorene
18	(C36) n-Hexatriacontane	Indeno[1,2,3-cd]pyrene
19	(C38) n-Octatriacontane	Naphthalene
20		Phenanthrene
21		Pyrene

GC-MS Conditions:

Parameter	Conditions
GC-MS system	Thermo Trace 1300 GC & ISQ MS
GC column	Restek Rxi®-5sil MS, 30m x 0.25mm, 0.25µm with Integra-Guard
GC liner	4 mm split liner with deactivated glass wool
Injection	1 µL split (1:100) at 300°C
Carrier gas	Ultra-high purity Helium at a constant flow of 1.2 mL/min
Oven temp. program	Initial temperature at 50°C, hold for 3 min; ramp at 10°C/min to 320°C, hold for 10 min
Temperatures	Transfer line = 275°C; Ion source = 275°C
Full scan range	35 - 600 amu

GC-FID Conditions:

Parameter	Conditions
GC-FID system	HP5890 Series II
GC column	Restek Rrx®-5 MS, 30m x 0.32mm, 0.5µm
GC liner	4 mm split/splitless liner with deactivated glass wool
Injection	1 µL splitless at 280°C
Carrier gas	Ultra-high purity Helium at a constant flow of 1.3 mL/min
Oven temp. program	Initial temperature at 55°C, hold for 0.3 min; ramp at 10°C/min to 320°C, hold for 10 min
FID temp.	320°C
Make-up gas	Ultra-high purity Hydrogen at a constant flow of 30 mL/min
Air flow	350 mL/min

Note: Both GC-MS and GC-FID were used during the evaluation of the sorbent. Conditions for both GC systems is outlined above.

ENVIRO

GC-MS Chromatograms:

Hexane (Aliphatic) Fraction:

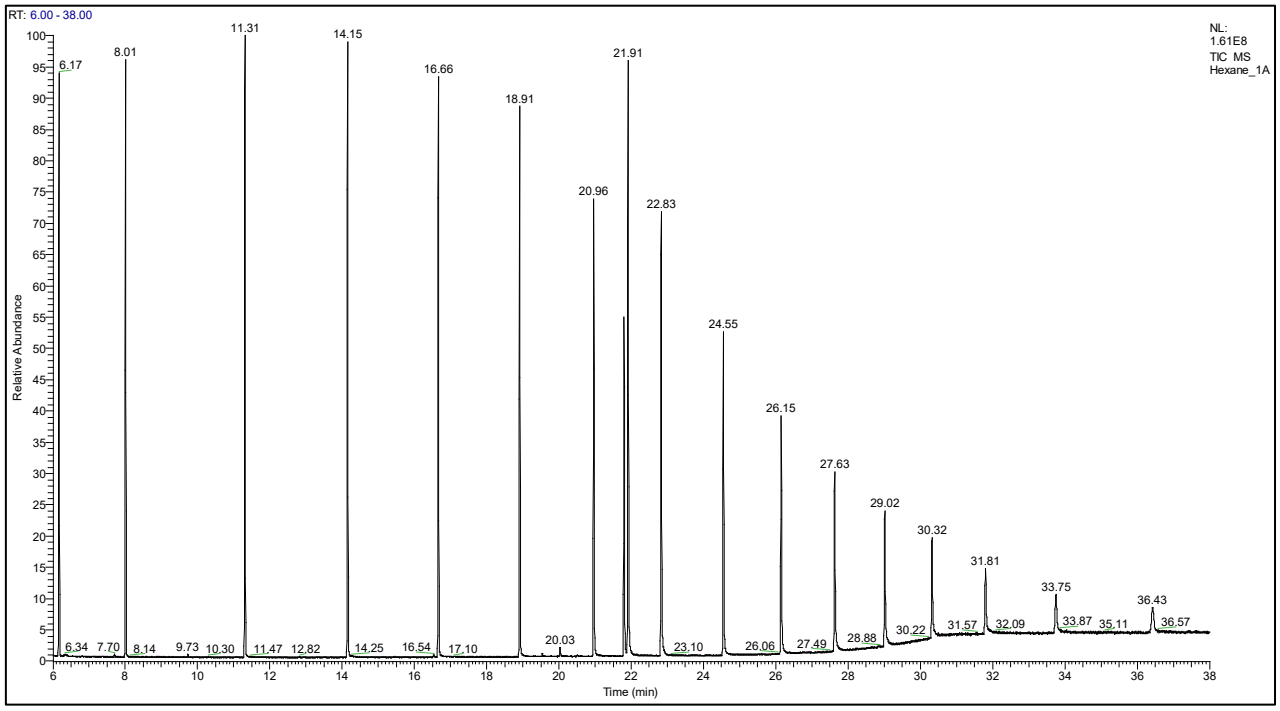


Fig. 1. Aliphatic fraction of a fractionation check sample fortified at 200 µg/mL (final conc. 50 of ug/mL).

Acetone (Aromatic) Fraction:

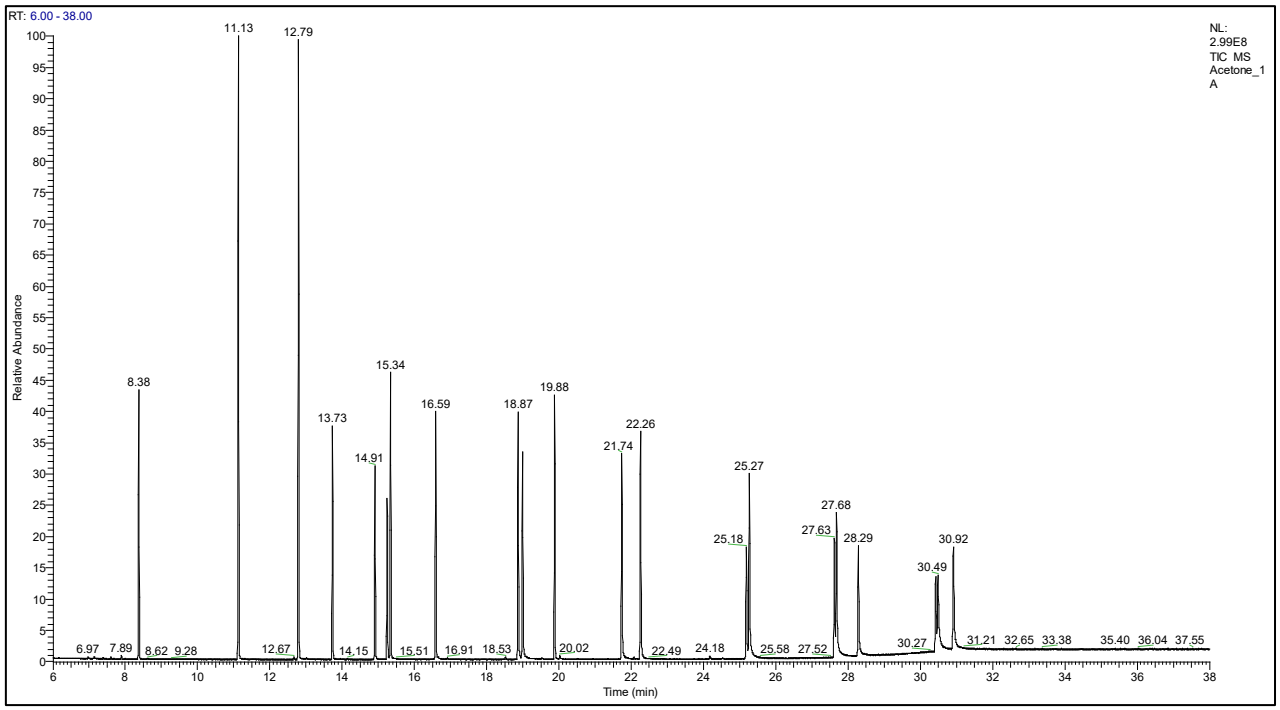


Fig. 2. Aromatic fraction of a fractionation check sample fortified at 200 µg/mL (final conc. of 50 ug/mL).

ENVIRO

GC-FID Chromatograms:

Hexane (Aliphatic) Fraction:

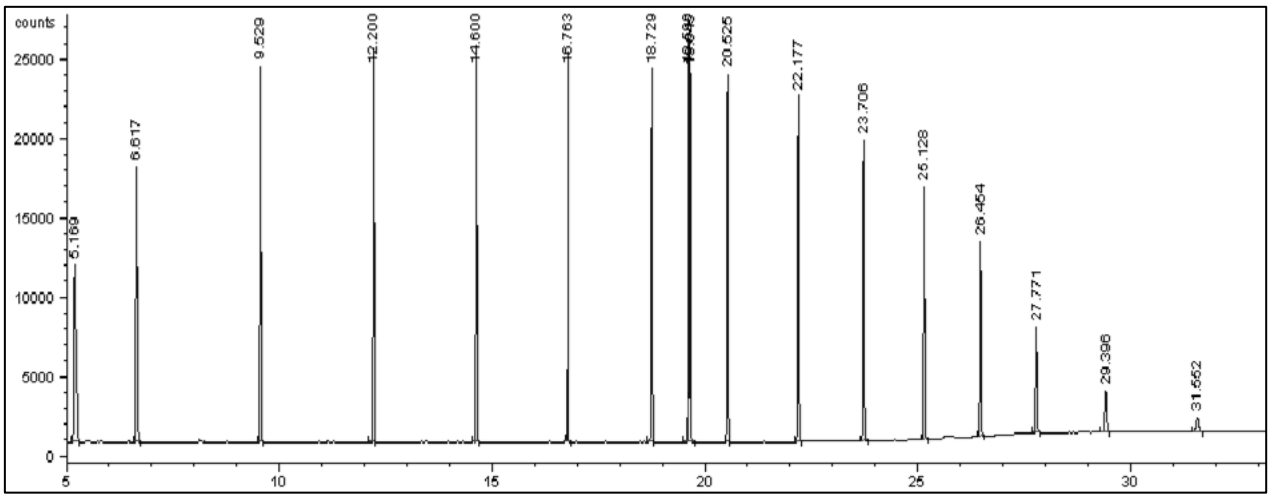


Fig. 3. Aliphatic fraction of a fractionation check sample fortified at 200 µg/mL (final conc. of 50 ug/mL).

Acetone (Aromatic) Fraction:

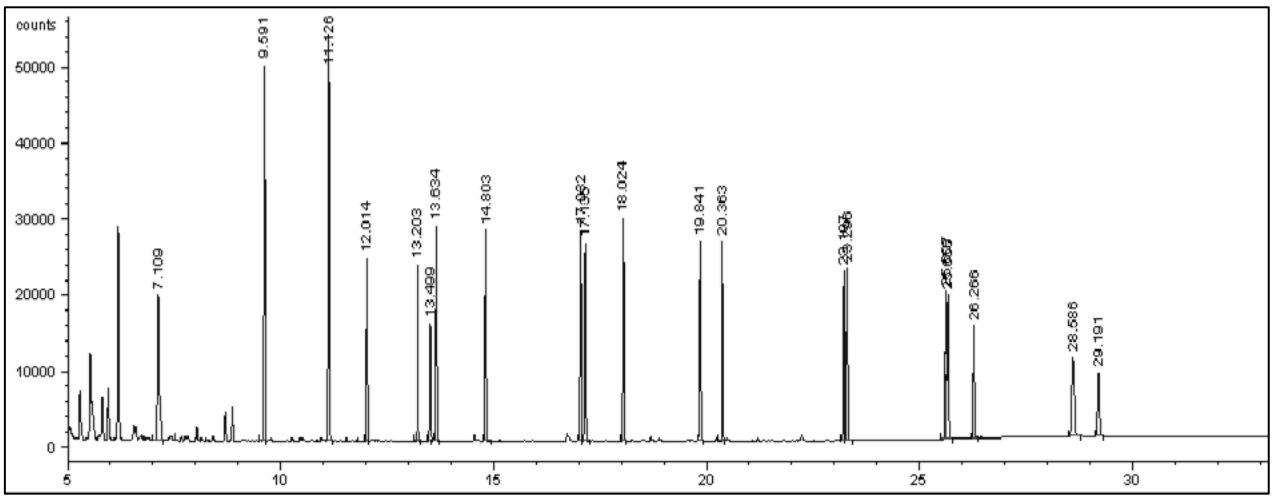


Fig. 4. Aromatic fraction of a fractionation check sample fortified at 200 µg/mL (final conc. of 50 ug/mL).

ENVIRO

Results:

Aromatics Recovery (%)	Sample 1	Sample 2	Sample 3	Sample 4	Mean	RSD (%)
o-Terphenyl (surr)	92	98	111	102	101	8.05
2-Bromonaphthalene (frac surr)	92	98	112	102	101	8.27
2-Fluorobiphenyl (frac surr)	93	98	112	103	101	8.07
2-Methylnaphthalene	92	97	111	101	100	8.15
Acenaphthene	83	87	98	91	90	7.24
Acenaphthylene	92	98	112	103	101	8.21
Anthracene	93	99	113	103	102	8.32
Benz[a]anthracene	91	97	111	102	100	8.34
Benzo[a]pyrene	91	94	106	99	97	6.98
Benzo[b]fluoranthene	91	97	112	103	101	8.74
Benzo[k]fluoranthene	90	96	110	100	99	8.48
Chrysene	91	97	111	102	100	8.57
Dibenz [a,h] anthracene	85	93	108	99	96	10.07
Dibenzo[ghi]perylene	86	94	108	99	97	9.83
Fluoranthene	90	96	109	100	99	8.13
Fluorene	92	97	111	102	100	8.22
Indeno[1,2,3-cd]pyrene	84	90	103	95	93	8.56
Naphthalene	108	115	136	124	121	9.89
Phenanthrene	91	97	111	101	100	8.20
Pyrene	91	97	112	102	101	8.52

Aliphatics Recovery (%)	Sample 1	Sample 2	Sample 3	Sample 4	Mean	RSD (%)
1-Chlorooctadecane (surr)	92	92	95	95	93	1.69
(C9) n-Nonane	96	97	99	98	98	1.37
(C10) n-Decane	96	97	99	98	98	1.31
(C12) n-Dodecane	98	98	100	100	99	1.21
(C14) n-Tetradecane	96	97	99	98	98	1.27
(C16) n-Hexadecane	95	96	98	98	97	1.56
(C18) n-Octadecane	91	92	94	94	93	1.67
(C19) n-Nonadecane	93	93	96	96	94	1.64
(C20) n-Eicosan	111	112	119	119	115	3.71
(C22) n-Docosane	91	92	94	94	93	1.74
(C24) n-Tetracosane	87	88	90	90	89	1.76
(C26) n-Hexacosane	89	89	92	92	90	1.80
(C28) n-Octacosane	87	88	90	90	89	1.84
(C30) n-Triacontane	82	83	85	85	84	1.92
(C36) n-Hexatriacontane	80	80	83	84	82	2.53

Lot-To-Lot Reproducibility:

Recovery (%)	Batch 1 (n=3)		Batch 2 (n=3)		Batch 3 (n=3)		Overall (n=9)	
Aromatics	**Mean**	**RSD**	**Mean**	**RSD**	**Mean**	**RSD**	**Mean**	**RSD**
o-Terphenyl (surr)	104	3.30	108	4.80	105	2.16	**106**	**3.52**
2-Bromonaphthalene (frac surr)	103	2.90	106	2.13	102	1.54	**104**	**2.74**
2-Fluorobiphenyl (frac surr)	108	4.42	112	1.98	110	2.64	**110**	**3.01**
1,2,3-Trimethylbenzene	106	3.21	107	2.55	105	1.11	**106**	**2.32**
2-Methylnaphthalene	105	2.92	108	1.07	106	1.17	**106**	**2.03**
Acenaphthene	105	2.97	107	2.79	105	1.35	**106**	**2.50**
Acenaphthylene	103	2.27	104	3.98	103	1.03	**103**	**2.42**
Anthracene	90	2.26	93	4.48	90	0.92	**91**	**3.04**
Benzo[a]anthracene	85	2.25	86	2.84	82	1.86	**84**	**2.73**
Benzo[a]pyrene	86	1.00	86	3.50	83	2.06	**85**	**2.83**
Benzo[b]fluoranthene	89	11.21	82	2.31	80	1.62	**84**	**7.85**
Benzo[ghi]perylene	86	2.88	87	2.31	85	0.79	**86**	**2.35**
Benzo[k]fluoranthene	82	1.79	83	1.79	77	0.11	**81**	**3.59**
Chrysene	91	3.19	94	3.28	90	2.46	**92**	**3.40**
Dibenz[a,h]anthracene	82	1.86	83	1.04	81	2.94	**82**	**2.28**
Fluoranthene	95	3.30	97	3.86	95	1.80	**96**	**3.06**
Fluorene	104	3.48	107	3.19	104	0.34	**105**	**2.72**
Indeno[1,2,3-cd]pyrene	75	1.72	75	1.78	72	0.85	**74**	**2.67**
Naphthalene	108	3.34	111	0.11	108	1.29	**109**	**2.08**
Phenanthrene	103	3.24	107	2.66	103	2.09	**104**	**2.90**
Pyrene	93	2.73	96	3.06	93	0.96	**94**	**2.67**

Recovery (%)	Batch 1 (n=3)		Batch 2 (n=3)		Batch 3 (n=3)		Overall (n=9)	
Aliphatics	**Mean**	**RSD**	**Mean**	**RSD**	**Mean**	**RSD**	**Mean**	**RSD**
1-Chlorooctadecane (surr)	84	0.73	83	1.73	83	0.65	**83**	**1.06**
(C9) n-Nonane	98	1.08	99	0.67	99	0.21	**99**	**0.90**
(C10) n-Decane	97	0.93	99	0.75	99	0.46	**98**	**1.04**
(C12) n-Dodecane	92	1.29	94	0.64	94	0.25	**94**	**1.32**
(C14) n-Tetradecane	93	1.69	93	0.30	93	0.77	**93**	**1.02**
(C16) n-Hexadecane	84	1.25	85	0.45	84	0.88	**85**	**1.00**
(C18) n-Octadecane	85	1.20	85	1.03	85	0.62	**85**	**0.89**
(C20) n-Eicosan	89	1.29	89	0.24	90	0.76	**90**	**0.78**
(C21) n-Heneicosane	90	1.50	89	1.10	90	1.11	**90**	**1.19**
(C22) n-Docosane	89	0.98	89	0.54	89	0.40	**89**	**0.62**
(C24) n-Tetracosane	89	1.07	89	0.26	90	0.81	**90**	**0.85**
(C26) n-Hexacosane	88	1.06	87	0.78	88	0.56	**88**	**0.82**
(C28) n-Octacosane	85	1.75	86	0.11	85	0.34	**85**	**0.95**
(C30) n-Triacontane	85	1.95	85	0.25	84	0.89	**85**	**1.12**
(C32) n-Dotriacontane	83	1.51	82	0.24	82	1.04	**83**	**1.04**
(C34) n-Tetratriacontane	81	1.31	79	1.01	80	1.09	**80**	**1.26**
(C36) n-Hexatriacontane	79	2.45	77	1.05	78	1.53	**78**	**1.97**
(C38) n-Octatriacontane	77	1.29	76	2.83	73	3.30	**75**	**3.08**

Conclusions:

This application note outlines the fractionation of hydrocarbons into aliphatic and aromatic fractions using UCT's new silver-phase EPH fractionation cartridges. The new SPE sorbent consists of silver ions functionalized onto a solid support. Aromatic hydrocarbons are selectively retained on the sorbent by forming a charge-transfer complex with the silver ions. This ensures high capacity for the aromatic hydrocarbons and no breakthrough into the aliphatic fraction.

Excellent analytical performance was obtained using the new fractionation cartridges and optimized SPE procedure. Recoveries were primarily in the 80 to 110% range with relative standard deviation (RSD) less than 10%. The results obtained comfortably passed the QC requirements laid out in the MADEP EPH method: recovery of 40 - 140% and RSD < 25%. There was no observed breakthrough of naphthalene and 2-methylnaphthalene into the aliphatic fraction, which also meets the required <5% breakthrough requirement.

Consistent lot-to-lot reproducibility without the need to optimize the elution solvent for each batch of cartridges are two major advantages of this new sorbent. In addition, the fractionation protocol is easier, faster, and uses less solvent than silica cartridges, while the use of acetone instead of dichloromethane as the elution solvent for the aromatic fraction is significantly more environmentally friendly. Finally, the high capacity of the sorbent relative to silica also opens the possibility of automating the fractionation process to improved day-to-day reproducibility and increased sample throughput.

References:

1. Method for the determination of extractable petroleum hydrocarbons (EPH). Massachusetts Department of Environmental Protection, Division of Environmental Analysis, Office of Research and Standards, Bureau of Waste Site Cleanup, Revision 1.1, May 2004.
2. Extractable Petroleum Hydrocarbons Methodology (Version 3.0). New Jersey Department of Environmental Protection, Site Remediation Program, Document number NJDEP EPH 10/08, August 2010, Revision 3.

UCT, LLC • 2731 Bartram Road • Bristol, PA 19007 800.385.3153 • 215.781.9255
www.unitedchem.com Email: methods@unitedchem.com

ENVIRO

UCT