

Introduction

Greater public concern about the long term health effects of exposure from leaking underground petroleum storage tanks has been addressed by both the US EPA and International environmental groups. The Massachusetts Department of Environmental Protection was one of the earliest to develop a comprehensive method for the qualitative identification of extractable petroleum hydrocarbons (EPH) or for the fractionation, detailed analysis, and quantitation of both aliphatic and aromatic fractions from site samples of water or soil/sediment matrices. This detailed quantitative analysis ensures optimal identification of suspected contaminants and also supports toxicological assessment for human exposure and was recently updated to Revision 1.1 in May 2004¹. Because of the broad and thorough nature of the quantitative information generated, many site managers and engineering firms request this method to be used, even for their out of state samples. In addition, some states, such as Texas², have adopted similarly detailed methods.

In these methods, heavily contaminated samples require initial liquid/liquid extraction into methylene chloride, evaporation, reconstitution and then fractionation and clean up using large 5 gram silica gel solid phase extraction (SPE) cartridges. Although these cartridges are now commercially available from many suppliers, the quality of these products must be assured with each lot and sometimes even within lots. The activity level and capacity of the silica used in the cartridge, the compression of the bed itself and the quality of the constituents and packaging used in the product are all critical to getting good results.

This study was designed to examine the factors necessary to reduce background contamination and coextractables, improve fractionation and reproducibility of extraction results and to verify adequate capacity for the recovery of all the analytes.

Experimental Conditions and Results

Background and Coextractables – SPE

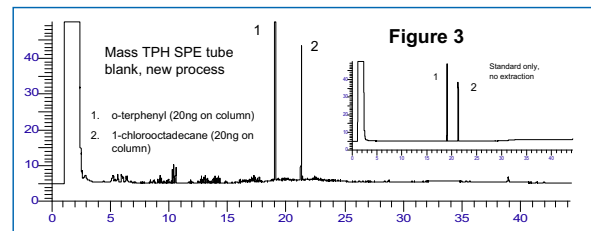
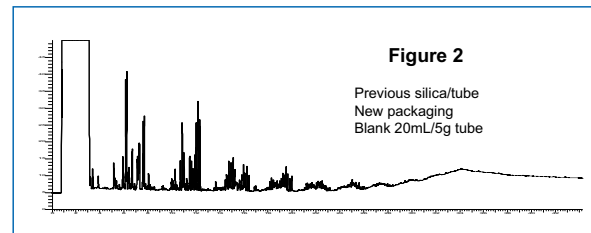
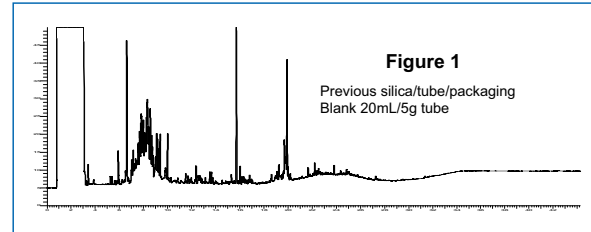
Extraction Conditions

- 20mL polypropylene, 5g

Cartridges extracted with 15mL of hexane, without prior conditioning. The hexane extract was dried by gentle nitrogen purge to 1mL and analyzed as a tube blank.

Analytical Conditions

- Column: Rtx-5 30m, 0.32 ID, 0.25µm (cat. #10224)
Inj.: 0.5µL splitless (hold 0.75 min), Restek PSSI Split/Splitless inlet liner with wool (cat.#21718)
Inj. temp.: 290°C
Inj. press. prog.: pressure pulse to 20psi @ -0.71min, pressure to 8psi @ 1.2min
Carrier gas: helium, constant pressure
Oven temp.: 60°C (hold 1 min.) to 310°C @8°C/min. (hold for 12 min.)
Det.: PerkinElmer Clarus GC-FID @ 330°C



Results for Background and Coextractables

- Coextractables may be found in the packaging, cartridge materials such as the tube and frits, and the silica itself.
- Processes have been refined to minimize all manufacturing contributions to background levels of extractables from these cartridges.
- When cartridges are received with low background levels, pre-cleaning steps with methylene chloride should be eliminated from routine lab procedures.

Fractionation – SPE

Extraction Conditions

- 20mL polypropylene, 5g
- Conditioning
 - 30mL hexane only
 - 200 or 500uL of water or methanol followed by 30mL hexane
- Extraction
 - 18mL hexane, dried down with gentle nitrogen purge to 1mL. for analysis.

Analytical Conditions – same as background runs

Aromatic Fraction, % Breakthrough with Excess Moisture/Solvent

	Active silica, nothing added	200uL water	500uL water	200uL methanol	500uL methanol
naphthalene	0.0	0.0	0.0	0.0	4.5
2-methylnaphthalene	0.0	0.0	0.0	0.0	0.0
2-fluorobiphenyl(surr)	0.0	0.0	0.0	0.0	0.0
acenaphthylene	0.0	0.0	0.0	0.0	0.0
2-bromonaphthalene (surr)	0.0	4.4	2.7	13.1	28.5

Effect of Ambient Moisture on Silica Fractionation Performance

surrogates	Lot A, new	Lot B, 1yr old	Lot C, 2 yr. old
	% recovery Hexane fraction	% recovery Hexane fraction	% recovery Hexane fraction
2-fluorobiphenyl	0.0	0.0	0.0
2-bromonaphthalene	0.0	33.3	28.5

Results for Fractionation

- The volume of hexane required to fractionate only the aliphatic portion of the sample without allowing the breakthrough of the more sensitive analytes into the second methylene chloride/aromatics fraction is determined by the activity level of the silica.
- Variations in the humidity levels during manufacture, storage or exposure of the cartridges in the lab, can have a dramatic effect on the fractionation results. Even very small volumes of residual solvent (as during pre-cleaning of the SPE cartridge with CH₂Cl₂) can cause early breakthrough of aromatics.
- Volume of hexane needed for optimal fractionation must be determined for each lot of silica used and checked whenever ambient lab conditions change.
- All cartridges should be left in original packaging until needed for extraction and unused tubes immediately re-sealed and stored in a dessicator.

Recovery/Reproducibility - SPE

Extraction Conditions

- 6mL glass, 2g
- 15mL high purity polypropylene, 3g
- 20mL polypropylene, 5g
- 80mL large diameter polypropylene, 5g
- Conditioning
 - 30mL hexane only
- Extraction
 - Hexane, various volumes, to elute aliphatic fraction
 - CH₂Cl₂, various volumes, to elute aromatic fraction
 - Each fraction collected separately and dried down with gentle nitrogen purge to 1mL. for analysis.
- Sample
 - 0.5mL MA Fraction Check mix [25ug/mL] (cat#31481), 0.5mL MA Fractionation Surrogate Spike mix [40ug/mL] (cat#31480) and 0.05mL MA EPH Surogate Spike mix [400ug/mL] (cat#31479)

Analytical Conditions – same as background runs

Recovery Table I

6mL, 2g glass	aliphatic		aromatic	
	3mL hexane % recov	6mL CH2Cl2 % recov	3mL hexane % recov	6mL CH2Cl2 % recov
nonane (C9)	14.0	73.4	70.0	
decane (C10)	13.9	83.8	76.8	
naphthalene		93.4		83.4
dodecane (C12)	15.3	79.0	80.5	4.3
2-methylnaphthalene		93.4		84.1
2-fluorobiphenyl (surrog)		93.3		85.5
tetradecane (C14)	17.2	77.6	81.8	5.2
acenaphthylene		94.5		84.4
2-bromonaphthalene (surrog)		94.2		90.7
acenaphthene		94.8		85.8
fluorene		94.3		82.7
hexadecane (C16)		76.5	85.7	4.8
phenanthrene		99.6		91.3
octadecane (C18)		77.2	91.3	
anthracene		99.7		88.5
nonadecane (C19)		81.4	91.1	5.5
o-terphenyl (IS)		99.3		88.4
eicosane (C20)	22.6	75.5	89.8	5.3
fluoranthene		100.2		85.9
1-chlorooctadecane (IS)		88.7	76.3	20.0

Recovery Table II

15mL, 3g	aliphatic		aromatic	
	8mL hexane % recov	8mL CH2Cl2 % recov	12mL hexane % recov	10mL CH2Cl2 % recov
nonane (C9)	85.8		91.8	
decane (C10)	84.6	26.4	91.2	
naphthalene		91.8	46.3	51.0
dodecane (C12)	86.4		91.4	
2-methylnaphthalene		93.0	31.3	66.1
2-fluorobiphenyl (surrog)		94.7		105.0
tetradecane (C14)	87.2		91.7	
acenaphthylene		95.4		104.4
2-bromonaphthalene (surrog)	8.0	88.1	79.0	13.9
acenaphthene		96.8	9.9	91.3
hexadecane (C16)	87.2		90.7	
fluorene		95.3		105.7
octadecane (C18)	89.3		87.2	
phenanthrene		99.8		103.1
anthracene		100.0		101.8
nonadecane (C19)	89.9	7.1	86.7	
o-terphenyl (IS)		96.6		105.9
eicosane (C20)	84.9		85.1	
1-chlorooctadecane (IS)	79.9		88.2	

Recovery Table III

80mL, 5g	aliphatic		aromatic	
	9mL hexane % recov	20mL CH2Cl2 % recov	19mL hexane % recov	20mL CH2Cl2 % recov
nonane (C9)	33.6	41.1	57.1	
decane (C10)	35.9	42.9	61.6	
naphthalene		73.0	36.7	13.8
dodecane (C12)	38.1		62.7	3.5
2-methylnaphthalene		76.2	35.4	15.6
2-fluorobiphenyl (surrog)		76.6	19.1	23.4
tetradecane (C14)	38.6	43.0	62.9	3.5
acenaphthylene		78.0	18.6	21.8
2-bromonaphthalene (surrog)		73.8	44.4	10.1
acenaphthene		74.6	26.5	17.5
hexadecane (C16)	39.3	42.1	66.7	7.5
fluorene		77.3	5.1	71.0
octadecane (C18)	41.2	43.4	70.0	6.5
phenanthrene		79.6	5.4	71.3
anthracene		80.3	8.1	68.1
nonadecane (C19)	42.4	44.2	72.8	7.0
o-terphenyl (IS)		82.7		86.3
eicosane (C20)	43.3	43.8	73.9	7.2
1-chlorooctadecane (IS)	12.7	72.1	75.9	11.7

Results for Recovery and Reproducibility

- Variations in silica activity, bed weight and packing bed geometry will have an effect on the fractionation and quantitative recovery of aliphatic and aromatic fractions
- Initial results do not support going to a larger diameter (80mL/5g), which would make elutions more rapid, unless the bed weight can also be increased.
- Narrower diameter tubes (15mL and 6mL) have practical limitations to the bed weight they can currently contain and elution times could become very slow. Optimum solvent volumes for fractionation using these sizes could not be determined in this study.
- Fractionation, recovery and reproducibility were easily optimized for the new process 20mL/5g cartridge.

Recovery Table IV

20mL, 5g	18mL hexane			20mL CH2Cl2		
	% recovery	std. deviation	RSD (n=4)	% recovery	std. deviation	RSD (n=4)
nonane (C9)	86.4	9.1	10.5			
decane (C10)	84.7	7.2	8.5			
naphthalene				82.3	6.1	7.4
dodecane (C12)	83.8	8.3	9.9			
2-methylnaphthalene				89.1	5.5	6.2
2-fluorobiphenyl (surrog)				92.1	6.7	7.3
tetradecane (C14)	90.7	6.3	6.9			
acenaphthylene				91.6	7.6	8.3
2-bromonaphthalene (surrog)				84.9	6.8	8.0
acenaphthene				93.4	6.3	6.8
fluorene				92.4	6.2	6.7
hexadecane (C16)	90.9	4.4	4.8			
phenanthrene				90.4	5.6	6.1
octadecane (C18)	94.9	3.4	3.6			
anthracene				91.5	5.3	5.8
nonadecane (C19)	91.1	3.6	4.0			
o-terphenyl (IS)				96.4	3.4	3.6
eicosane (C20)	89.8	2.6	2.9			
fluoranthene				93.4	3.2	3.4
1-chlorooctadecane (IS)	83.1	5.0	6.0			
pyrene				95.1	3.8	4.0
docosane (C22)	85.2	4.0	4.7			
tetracosane (C24)	85.0	3.2	3.8			
benzo(a)anthracene				91.2	2.4	2.6
chrysene				90.9	2.6	2.8
hexacosane (C26)	85.8	3.0	3.5			
octacosane (C28)	85.7	2.5	2.9			
benzo(b)fluoranthene				91.3	2.2	2.4
benzo(k)fluoranthene				90.8	2.1	2.3
benzo(a)pyrene				91.0	2.7	2.9
triacentane (C30)	86.0	2.5	2.9			
dibenzo(a,h)anthracene				90.9	1.8	2.0
indeno(1,2,3-cd)pyrene				91.4	1.5	1.6
benzo(g,h,i)perylene				90.7	2.2	2.4
hexatriacene (C36)	78.6	4.0	5.0			

Conclusions

- Improved manufacturing processes have resulted in low background silica cartridges.
- These cartridges have excellent fractionation, recovery and reproducibility results when used with the current Massachusetts EPH Method Revision 1.1
- Other cartridge sizes, geometries, silica types and weights did not result in improved backgrounds, fractionation or recovery results.

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. Total Petroleum Hydrocarbons, TNRCC Method 1005, Revision 03 (June 1, 2001); Draft TNRCC Method 1006 (May 2000) Texas Natural Resource Conservation Commission.