Superior Fractionation of Extractable Petroleum Hydrocarbons

Get More Accurate Results Using Restek SPE Tubes

By Lydia Nolan, Innovations Chemist

- Easier quantitation; lower background & less interference.
- Reliable, reproducible results.
- Unique packaging designed for convenience and storage stability.

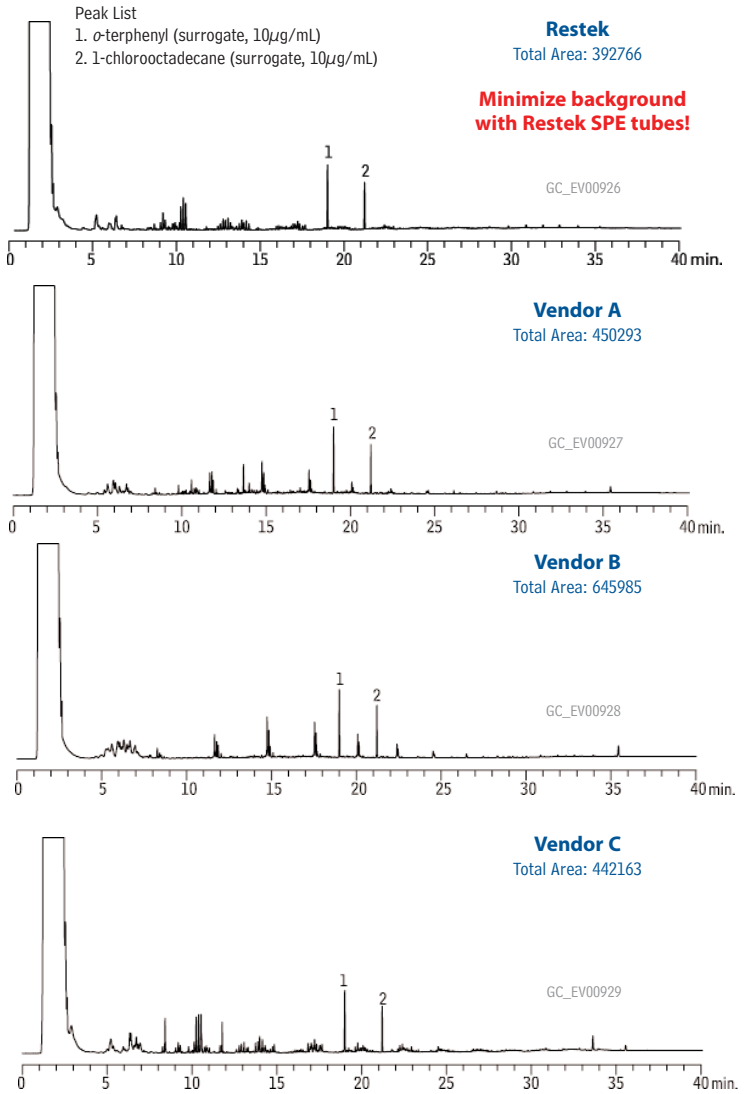
There is an increasing public awareness of the threat to public health from leaking underground storage tanks. Both federal and state agencies have developed methods to address the testing of potential problem sites. The Massachusetts Department of Environmental Protection's "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" has recently been updated and is based on solvent extraction of water and soil/sediment matrices, followed by silica gel SPE fractionation of aliphatics and aromatics from C9 through C36 hydrocarbon ranges.

The quality and conformation of the silica SPE clean-up column is essential to acceptable fractionation and recovery results. Commercial silica SPE products streamline this process, but it is important to understand the quality and performance differences among the available products, and the impact they have on your results. The activity level and capacity of the silica, the compression of the bed, and the quality of the constituents and packaging are all critical to getting accurate and reliable results. The data in Table I show how even very minor amounts of excess moisture (known amounts added for experimental purposes during the first conditioning step) or long-term storage without desiccation can produce early breakthrough of the sensitive analytes from the aromatic fraction into the aliphatic fraction.

To ensure maximum shelf-life and minimum environmental exposure after opening these cartridges, Restek packages them into 5 smaller packs of 4 SPE tubes each—the fewest cartridges per pack available. We also provide an additional outer, resealable barrier bag, making successful short- and long-term product storage easier for the user.

Activity level of the silica and consistency of the cartridge packing are essential for reliable fractionation recovery and reproducibility. The recovery and reproducibility of results for the fractionation surrogates (2-fluorobiphenyl, 2-bromonaphthalene and naphthalene) are critical to determining if breakthrough is occurring. Again, in comparing several commercial sources, using optimized conditions for each vendor, results show that the Restek Massachusetts EPH cartridges are capable of quantitative (greater than 97%) and reliable (RSDs less than 7.3) recoveries for these critical markers (Table II).

Figure 1 Restek Massachusetts EPH SPE tubes show the lowest overall level of background response.



Column: Rtx®-5, 30m, 0.32mm ID, 0.25µm (cat.# 10224)
Sample: Massachusetts EPH Surrogate Spike Mix (4000µg/mL each component) diluted to 400µg/mL in hexane.
Spiking standard: 50µL Inj.: 0.5µL, splitless (hold 0.5 min.), PSS split/splitless inlet liner (cat.#21717)
Inj. temp.: 280°C; Carrier gas: helium, constant velocity; Pressure pulse program: 50cm/sec @ -0.71 min., split ratio = 0 @ -0.70 min., split ratio = 20:1 @ 0.75 min., 35cm/sec @ 0.8 min.; Linear velocity: 35cm/sec
Oven temp.: 60°C (hold 1 min.) to 310°C @ 8°C/min. (hold 12 min.), Det.: FID @ 330°C

* Total area counts exclude response for solvent front and surrogate peaks
1. o-terphenyl (surrogate) 10ng on-column
2. 1-chlorooctadecane (surrogate) 10ng on-column
All cartridges were extracted with 15mL hexane, without prior conditioning. Extract blanks were then spiked with the 50µL of MA EPH Surrogate Spike mix, cat#31479 (diluted to 400µg/mL with hexane), and dried down to 1mL with gentle nitrogen purge.

Table I Excess moisture and improper storage compromise results by causing breakthrough into the aromatic fraction.

	% Breakthrough into Hexane (Aliphatic) Fraction			
Analyte	Package intact, no added moisture	200µL water added	Package opened, resealed, stored on shelf, 1 year	Package intact, stored on shelf, 1 year
Naphthalene	0.0	0.0	----	----
2-fluorobiphenyl (surrogate)	0.0	0.0	----	----
2-bromonaphthalene (surrogate)	0.0	4.4	33.3	28.5

Table II Restek Massachusetts EPH SPE tubes provide more accurate and reproducible results for critical marker compounds.

	Restek			Vendor A			Vendor B			Vendor C		
Analyte	percent recovery	STD	%RSD	percent recovery	STD	%RSD	percent recovery	STD	%RSD	percent recovery	STD	%RSD
naphthalene	103.1	7.5	7.2	101.2	10.1	10.0	88.8	2.8	3.1	66.5	2.6	3.9
2-fluorobiphenyl	97.8	6.6	6.7	100.4	13.7	13.6	99.3	5.0	5.0	104.2	6.6	6.4
2-bromonaphthalene	98.6	5.3	5.4	71	7.1	10.0	50.0	8.1	16.1	29.2	1.9	6.6

All tubes were 20 or 25mL with approximately 5g silica packing. Conditioning: 15mL hexane. Sample: 0.5mL of each fractionation check standard and surrogate standard. Elution for fraction #1 (aliphatics): 17-20mL hexane (volume was optimized for each supplier and lot of tubes). Elution for fraction #2 (aromatics): 20mL of CH_2Cl_2. Each fraction was dried to a total volume of 1mL and analyzed by GC.[1]

Coextractables are another major concern with commercial cartridges. The contaminants may be found in the packaging, cartridge materials such as the SPE tube and frits, and the silica itself. The solvent blank extractions shown in Figure 1 were collected from cartridges that were not pre-conditioned. Restek cartridges show the lowest level of background peak area counts, indicating the lowest level of background extractables.

When cartridges start out with low levels of extractables, it may not be necessary to use the methylene chloride pre-treatment allowed in the method. This pre-treatment can easily compromise the fractionation performance of the cartridge beds and should be avoided whenever possible. In addition, fewer product-related contaminants will provide clearer quantitation and require fewer manual reviews of the data generated from the final chromatograms.

In all of the key performance areas, the Restek Massachusetts EPH SPE tubes outperformed other commercially available products. Our cartridges are designed to deliver accurate, reliable, and reproducible results. For high quality separation products developed to prevent breakthrough and minimize background, reach for Restek sample preparation products.

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.

MA Fractionation Check Mix (31 components)

PAHs:	Hydrocarbons:
acenaphthene	*n*-nonane (C9)
acenaphthylene	*n*-decane (C10)
anthracene	*n*-dodecane (C12)
benzo(a)anthracene	*n*-tetradecane (C14)
benzo(a)pyrene	*n*-hexadecane (C16)
benzo(b)fluoranthene	*n*-octadecane (C18)
benzo(k)fluoranthene	*n*-nonadecane (C19)
benzo(ghi)perylene	*n*-eicosane (C20)
chrysene	*n*-docosane (C22)
dibenzo(a,h)anthracene	*n*-tetracosane (C24)
fluoranthene	*n*-hexacosane (C26)
fluorene	*n*-octacosane (C28)
indeno(1,2,3-cd)pyrene	*n*-triacontane (C30)
2-methylnaphthalene	*n*-hexatriacontane (C36)
naphthalene	
phenanthrene	
pyrene	

25µg/mL each in hexane, 1mL/ampul
cat. # 31481

MA Fractionation Surrogate Spike Mix

2-bromonaphthalene 2-fluorobiphenyl
4,000µg/mL each in hexane, 1mL/ampul
cat. # 31480

MA EPH Surrogate Spike Mix

1-chlorooctadecane *o*-terphenyl
4,000µg/mL each in acetone, 1mL/ampul
cat. # 31479

Method Specific SPE Cartridges: Massachusetts EPH

Tube Volume, Bed Weight	qty.	cat.#
20mL, 5g	20-pk.	26065

Rtx®-5 Columns (fused silica)

(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.32mm	0.25	-60 to 330/350°C	30-Meter	10224

Splitless Liners for PerkinElmer GCs

ID* x OD & Length (mm)	qty.	cat.#

for **more** info

For more information on our selection of SPE tubes, visit us online at **www.restek.com**