



Accurate, Reliable Fractionation of Extractable Petroleum Hydrocarbons

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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.

For this method and others, the quality and conformation of the silica SPE clean-up column is essential to obtaining acceptable fractionation and recovery results. Commercial silica SPE products streamline this process, but can vary in performance. Here we evaluate the background response levels of several commercially available SPE tubes and compare the accuracy and reproducibility of results generated using them under the revised Massachusetts EPH method.

Recovery and Reproducibility

The 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 other sensitive analytes, such as naphthalene, are critical to determining if breakthrough is occurring. 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 I).

Background Response

Coextractables are another major concern with commercial cartridges. 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 pretreatment allowed in the method. This pretreatment can easily compro-

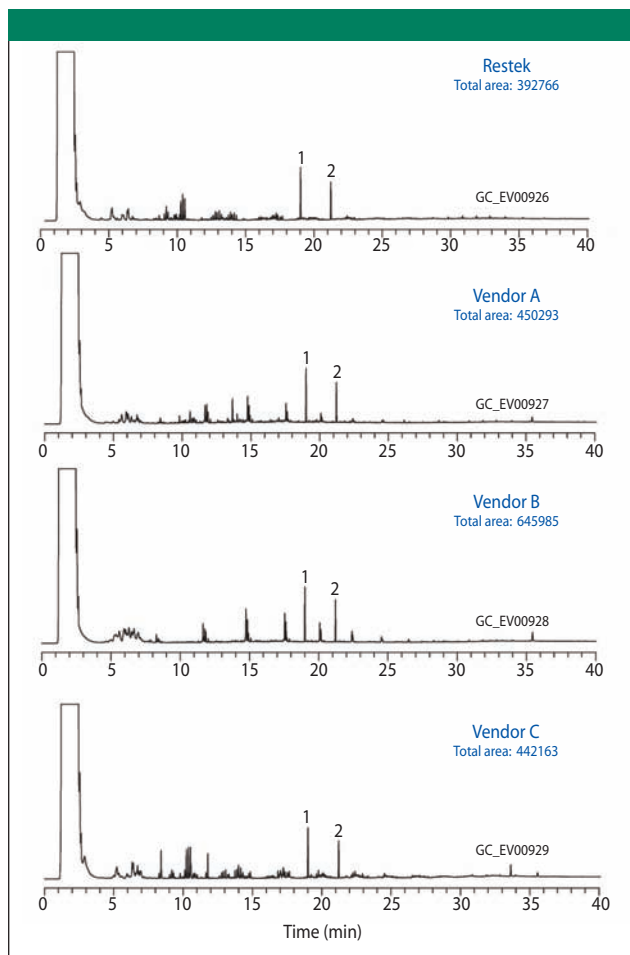


Figure 1: Comparison of background responses among SPE tubes from different vendors. Column: Rtx-5, 30 m, 0.32 mm i.d., 0.25 μm (cat.# 10224); Sample: Massachusetts EPH Surrogate Mix (4000 $\mu\text{g}/\text{mL}$ each component) diluted to 400 $\mu\text{g}/\text{mL}$ in hexane; Spiking standard: 50 μL ; Inj.: 0.5 μL , splitless (hold 0.5 min), PSS split/splitless inlet liner (cat.# 21717); Inj. temp.: 280 $^{\circ}\text{C}$; Carrier gas: helium, constant velocity; Pressure pulse program: 50 cm/s at -0.71 min, split ratio = 0 at -0.70 min, split ratio = 20:1 at 0.75 min, 35 cm/s at 0.8 min; Linear velocity: 35 cm/s; Oven temp.: 60 $^{\circ}\text{C}$ (hold 1 min) to 310 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$ (hold 12 min), det.: FID at 330 $^{\circ}\text{C}$. All cartridges were extracted with 15 mL hexane, without prior conditioning. Extract blanks were then spiked with the 50 μL of MA EPH Surrogate Spike mix, cat# 31479 (diluted to 400 $\mu\text{g}/\text{mL}$ with hexane), and dried down to 1 mL with gentle nitrogen purge. Peaks: 1 = o-terphenyl (surrogate) 10 ng on-column, 2 = 1-chlorooctadecane (surrogate) 10 ng on-column. Total area counts exclude response for solvent front and surrogate peaks.

Table I: Accuracy and reproducibility results for critical marker compounds

Analyte	Restek			Vendor A			Vendor B			Vendor C		
	percent recovery	STD	n = 3 RSD	percent recovery	STD	n = 3 RSD	percent recovery	STD	n = 3 RSD	percent recovery	STD	n = 3 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 25 mL with approximately 5 g silica packing. Conditioning: 15 mL hexane. Sample: 0.5 mL of each fractionation check standard and surrogate standard. Elution for fraction #1 (aliphatics): 17–20 mL hexane (volume was optimized for each supplier and lot of tubes). Elution for fraction #2 (aromatics): 20 mL of CH₂Cl₂. Each fraction was dried to a total volume of 1mL and analyzed by GC (1).

mise 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.

Conclusion

In the key performance areas tested, Restek Massachusetts EPH SPE tubes outperformed other commercially available products. These cartridges deliver accurate, reliable, and reproducible results. For high quality separation products developed to prevent breakthrough and minimize background, Restek sample preparation products are an excellent choice.

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.

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