

## An Improved Method for Diesel Fractionation Following the Revised Massachusetts EPH Guidelines

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### Introduction

Environmental contamination from fuel leaks or spills is of major concern across the USA. The main source of this contamination is from underground storage tanks (UST). These tanks are used to store gasoline, diesel, heating oil, kerosene, or jet fuel. Until the mid-1980s, UST were composed of steel and subjected to corrosion and subsequent leaking. New tank designs have significantly reduced the danger. However, faulty installation or inadequate operating and maintenance procedures continue to result in environmental contamination.

The identification of fuel oils in environmental labs is done under EPA total petroleum hydrocarbon (TPH) method 8015B. The semivolatile fraction is identified by the distribution pattern displayed when analyzed via GC-FID.

Since petroleum products are composed of over 250 identified compounds, it would be difficult, if not impossible, to analyze all constituents.

Some states, such as Massachusetts, have created separate methods for extractable petroleum hydrocarbons (EPH) and volatile petroleum hydrocarbons (VPH). The new EPH methods take a more toxicological approach to evaluate the composition of aliphatic and aromatic compounds within a sample. These compounds and compound classes have very different exposure limits. The fuel can be fractionated using silica gel and the aliphatic and aromatic groups analyzed separately using GC-FID. The toxicological potential can then be determined for each compound class, thus allowing for more accurate identification of the true health risk.

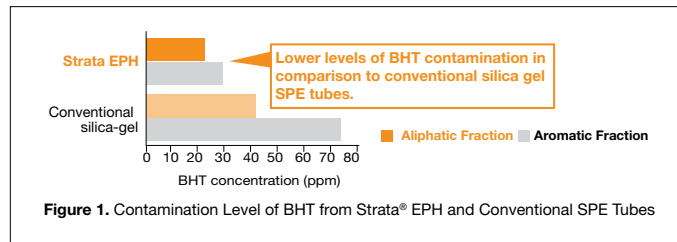


Figure 1. Contamination Level of BHT from Strata® EPH and Conventional SPE Tubes

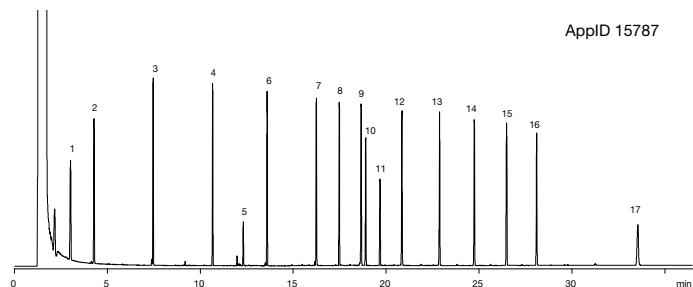


Figure 2. Representative chromatogram of the aliphatic fraction.

In this application, we present Strata® EPH, a specialized SPE sorbent designed to help overcome the challenges associated with traditional silica gel fractionation. Analysis was performed using a Zebron™ ZB-5ms GC column designed to provide optimal resolution of both aliphatic and aromatic fractions from surrogates and fractionation check compounds.

### Experimental Conditions

#### SPE Conditions

The Strata EPH (5 g/20 mL) cartridge was prewashed with 30 mL of hexane. 2 mL of EPH standard (Ultra Scientific, Kingstown, Rhode Island) containing a blank, 5 ppm, and 50 ppm sample of aliphatic, aromatic, and surrogates was loaded. All sampling was done in triplicates. The aliphatic fraction was eluted with 11 mL of hexane. The aromatic fraction was eluted with 20 mL of methylene chloride. Samples were concentrated to a final volume of 1 mL and analyzed by GC.

#### GC Analysis

Analysis was performed using a Zebron ZB-5ms, 30 m x 0.32 mm x 0.25 µm column (Phenomenex, Inc., Torrance, CA, USA). The initial oven program was 60 °C held for 1 min, then ramped to 290 °C at 8 °C/min and held for 6.75 min. Inlet temperature was set at 280 °C with helium carrier gas flow set at 3 mL/min operated in constant flow mode. A 2 L splitless injection was made. The detector temperature was set at 315 °C.

### Results and Discussion

The testing procedure was designed to meet the new Massachusetts EPH revision 3 (MAEPH3) testing procedure. The main goal of this work was to provide an extraction and analysis procedure that would reduce the time necessary to process each sample.

Strata EPH sorbent was specially designed to provide fast, consistent flow rates while still maintaining high recovery and efficient fractionation. The increased flow rate allowed processing

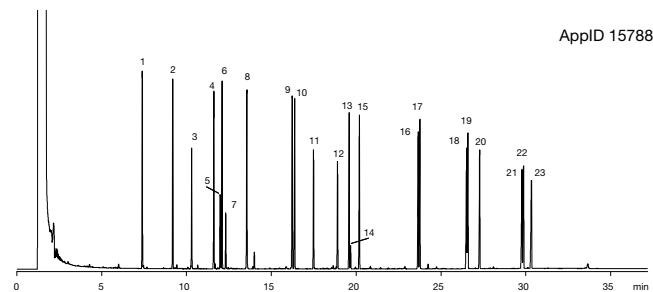


Figure 3. Representative chromatogram of the aromatic fraction.



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time to be reduced from 50 min to only 26 min. This translated to 50 % increase in productivity, allowing at least two times more samples to be processed each hour.

An added benefit to the fast flow rate is the solvent spends less time in contact with the SPE tubes, thus reducing contamination of butylated hydroxytoluene (BHT), a plasticizer found in SPE tubes. Most SPE tubes are composed of polypropylene, a medical grade of plastic that is inert to most sample matrices. However, the tube material has been shown to leach plasticizers when exposed to halogenated solvents such as methylene chloride. Conventional SPE tube materials showed BHT levels up to 75 ppm, however the Strata EPH tubes showed less than 40 ppm (Figure 1).

Although flow rates were dramatically increased, this did not affect the recoveries. The MAEPH3 method required 40–140 % recovery of all target compounds, with the exception of n-nonane (C9). The present work demonstrated 88 % recovery for the aliphatic fraction compounds at both the 5 ppm and 50 ppm levels (Tables 1 and 2). Recoveries for all compounds were greater than 88 %, including n-nonane.

The aromatic fraction recoveries were all above 67 %, with a majority of compounds above 85 %. Naphthalene and 2-methylnaphthalene are subject to reduced recoveries due to bleed into the aliphatic fraction and loss by evaporation. The method requires the aliphatic fraction to be monitored on a sample batch basis to ensure breakthrough concentration is less than 5 % for each compound. Breakthrough of both naphthalene and 2-methylnaphthalene were calculated at 3.60 % and 2.93 %, respectively.

Once fractionation conditions have been met, MAEPH3 requires GC performance standards to be optimized. The first step is to resolve all target peaks from each other and from the internal standards and surrogates. The method calls for a 5 %-phenyl–95 %-dimethylpolysiloxane phase. We chose the Zebron ZB-5ms column because the phase provides enhanced resolution of PAH isomers allowing for more accurate quantitation.

All compounds in the aliphatic fraction were resolved to baseline from contaminants, internal standards, and surrogates, including n-nonane from the solvent front. There was also baseline resolution between n-dodecane and the breakthrough of naphthalene.

Baseline resolution of PAH isomers is required for all but the following pairs of compounds: benz[a]anthracene and chrysene, benzo[b]fluoranthene and benzo[k]fluoranthene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene. Those compounds are to be separated such that the valley between the two peaks is less than 25 % of the average height of the two peaks. This standard was exceeded for all compounds.

## Conclusion

The new Strata EPH fractionation tubes used in conjunction with the Zebron ZB-5ms columns provide an application solution that can be implemented easily in labs looking to perform EPH testing.

## References

- (1) *FY 2005 Semi-Annual Mid-Year Activity Report* (U.S. Environmental Protection Agency, 2005).
- (2) *Method For The Determination of Extractable Petroleum Hydrocarbons (EPH)* (Massachusetts Department of Environmental Protection, Revision 1.1 May 2004).
- (3) "Leaking Underground Storage Tanks, Boulder Area Sustainability Information Network" (<http://bcn.boulder.co.us/basin/waterworks.html>).

**Table 1.** Aliphatic fraction data. RSD for C<sub>9</sub>-C<sub>18</sub> Class = 5.3 %. RSD for C<sub>18</sub>-C<sub>36</sub> Class = 3.8 %

Peak	Compound	% Recovery	% RSD (n=3)	Retention Time (min)	GC % RSD
1	n-Nonane (C9)	88.4	2.3	3.018	4.37
2	n-Decane (C10)	91.9	2.3	4.283	4.87
3	n-Dodecane (C12)	92.8	2.2	7.458	5.30
4	n-Tetradecane (C14)	93.2	2.2	10.662	5.67
5	Butylhydroxytoluene (BHT)			12.315	
6	n-Hexadecane (C16)	94.2	2.3	13.592	5.66
7	n-Octadecane (C18)	93.5	2.2	16.240	5.31
8	n-Nonadecane (C19)	91.1	1.9	17.473	5.11
9	n-Eicosane (C20)	92.8	1.9	18.648	5.10
10	5- $\alpha$ -Androstane (IS)			18.903	
11	1-Chloro-Octadecane (Surr)			19.671	
12	n-Docodane (C22)	92.9	1.8	20.848	4.75
13	n-Tetracosane (C24)	92.2	1.6	22.871	4.24
14	n-Hexacosane (C26)	92.4	1.6	24.741	3.47
15	n-Octacosane (C28)	93.4	1.5	26.478	2.65
16	n-Triacotane (C30)	95.9	1.4	28.098	2.29
17	n-Hexatriacontane (C36)	111.6	0.8	33.536	8.02

**Table 2.** Aromatic fraction data. RSD for aromatic = 8.8 %

Peak	Compound	% Recovery	% RSD (n=3)	Retention Time (min)	GC % RSD
1	Naphthalene	67.2	2.2	7.392	11.67
2	2-Methylnaphthalene	72.1	1.7	9.185	12.59
3	2-Fluorobiphenyl (Frac Surr)		1.0	10.307	
4	Acenaphthalene	72.9	1.3	11.602	13.12
5	2-Bromonaphthalene (Frac Sur)			11.985	
6	Acenaphthene	76.2	1.3	12.086	
7	Phthalate	97.9		12.313	13.24
8	Fluorene	92.8	2.2	13.544	13.14
9	Phanthrene	84.0	2.7	16.215	13.04
10	Anthracene	84.3	2.2	16.354	12.82
11	o-Terphenyl (Surr)			17.488	
12	5- $\alpha$ -Androstane			18.900	
13	Fluoranthene	84.1	2.2	19.568	13.23
14	1-Chloro-Octadecane (Surr-Aliphatic)			19.667	
15	Pyrene	88.3	2.2	20.169	10.24
16	Benz[a]anthracene	87.4	2.0	23.627	12.22
17	Chrysene	97.0	2.0	23.724	12.30
18	Benzo[b]fluoranthene	90.6	2.4	26.477	11.59
19	Benzo[k]fluoranthene	91.9	1.7	26.546	11.84
20	Benzo[a]pyrene	91.4	1.7	27.245	11.34
21	Indeno[1,2,3-cd]pyrene	94.8	1.1	29.732	10.62
22	Dibenz[a,h]anthracene	92.7	1.2	29.829	10.96
23	Benzo[g,h,i]perylene	90.5	1.1	30.274	10.58

## ORDERING INFORMATION

Part No.	Description
7HM-G010-11-TN	ZB-5ms, 30 m x 0.32 mm x 0.25 $\mu$ m
8B-S031-LEG-TN	Strata EPH Giga tube, 5 g/20 mL