An Automated Method for the Fractionation of Extractable Petroleum Hydrocarbons (EPH) from Water and Soil Extracts Using the Gilson GX-274 ASPEC™ System

Keywords: Aliphatic Hydrocarbons, Aromatic Hydrocarbons, Automation, Contaminants, EPH, Extractable Petroleum Hydrocarbons, GC/FID, GX-274 ASPEC, MADEP EPH Method, Petroleum Hydrocarbons, Silica Gel Fractionation, Soil, Solid Phase Extraction, SPE, Water

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Introduction

Crude and refined petroleum products contain a complex mixture of aliphatic and aromatic hydrocarbons as well as a variety of other compounds. The concentration of these different hydrocarbons will vary in different products such as crude oil, refined products and other residual oil products. Many of these hydrocarbons have been shown to pose a risk to human health or to aquatic life. Leaking underground storage tanks are a common source of groundwater and soil contamination. It is important to determine the types of hydrocarbons that may be present in contaminated soil and water.

Government agencies and other regulatory bodies have developed several methods for determining the types of aliphatic and aromatic hydrocarbons that may be found in contaminated soil or water. One such method is the "Method for the Determination of Extractable Hydrocarbons (EPH)" developed by the Massachusetts Department of Environmental Protection (MADEP, 2004). This method measures the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons (EPH) that may be found in a soil or water sample. The MADEP EPH Method utilizes a solvent extraction step followed by a silica gel fractionation into two extracts – an aliphatic extract (C_9–C_{18}, C_{19}–C_{36}) and an aromatic extract (C_{11}–C_{22}). The two extracts are then concentrated and separately analyzed by capillary gas chromatography with a flame ionization detector (GC/FID).

The Silica Gel Cleanup and Fractionation step of the method requires a great deal of care and attention to detail to achieve satisfactory results. A high degree of recovery and reproducibility are required for success. The automation of this step will reduce the opportunity for human error, reduce the use of solvents and generation of hazardous wastes and decrease the overall cost per test. This study describes an automated protocol for the fractionation of EPH into aliphatic and aromatic fractions using a Gilson GX-274 ASPEC™ System (Figure 1).

Figure 1. Gilson GX-274 ASPEC System (Part no. 2614010) with ASPEC System organizer (Part no. 21050000).

Experimental Conditions

Materials

All solvents were distilled in glass suitable for GC, HPLC, pesticide residues analysis and spectrophotometry. All reagents were ACS grade quality or better. Stock solutions of target petroleum blends (aromatic and aliphatic) were purchased from Absolute Standards, Inc. (Hamden, CT), Accustandard (New Haven, CT) or Aldrich (Milwaukee, WI). Biotage ISOLUTE® Silica gel cartridges, 1g/6 mL (Part no. 460-0100C) were used to fractionate EPH sample extracts. Surrogate standards, calibration solutions, matrix spiking solution and internal standards were prepared in accordance with the MADEP EPH Method. A Fractionation Check Standard is required to monitor the fractionation efficiency of the silica gel columns and system. This ensures that the optimal amount of hexane is used to prevent breakthrough of the hydrocarbon aromatics into the aliphatic hydrocarbon fraction. Each new lot of SPE cartridge was monitored using the fractionation check standard.

Preparation of Samples Prior to Automated Silica Gel Fractionation Step

Water samples are prepared in accordance to USEPA Method 3510 (separatory funnel liquid-liquid extraction). Soil samples were prepared in accordance to USEPA Methods 3540 (Soxhlet extraction) or 3546 (Microwave extraction).

Automated Silica Gel Fractionation Step

The Gilson GX-274 ASPEC System was configured as follows:

Description	Part numbers
GX-274 ASPEC	2614010
Four 10 mL Syringes	(4) 25025345
10 mL Plumbing Package for GX-274 ASPEC	2644705
Four 221 x 1.5 x 1.1 BV Tapered Probes and Guide Package for 1.5 mm Probes (GX-274)	(4)27067374 and 2604641
GX-274 Rinse Station and Rinse Station Riser	260440002 and 26045103
Solvent Reservoir Tray Insert for 700 mL bottles and pkg of four 700 mL solvent bottles	260440005 and 543701700
Locator Tray for five 20-Series Racks, GX-274	26041032
Two Custom SPE racks to hold 16 6 mL SPE cartridges and 32 collection tubes	(2) Special 1011: Custom Rack and 210630CR, TLH Rack File for Special 1011
Two Custom Racks to hold 56 15 x 45mm vials	(2) Special 1012: Custom Rack and 210630CR, TLH Rack File for Special 1012
Rack Code 343 for 80 13 x 100 mm tubes	260440025
Disposable sealing caps for 6 mL SPE cartridges, package of 1000	2954730
Glass collection tubes for 6mL DECs, 10mL (15 x 85 mm), package of 1000	2954729
Viton tubing, .313 ID x .438 OD, 20 ft	4701438630
Safety Shield Assembly, GX27X	2604706
TRILUTION LH Software Package	21063020, 210630R20 and ORACLE10GXE

The fractionation procedure used 1g/6 mL Biotage ISOLUTE™ Silica Gel Cartridges. The cartridges were sealed using Gilson 6 mL Sealing Caps.

The fractionation protocol is entirely automated using the Gilson GX-271 ASPEC system.
The SPE steps are summarized with the schematic provided in the GX-271 ASPEC control software, TRILUTION LH (Figure 2).

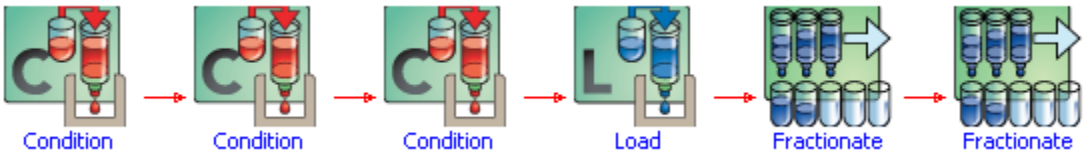

Figure 2. TRILUTION LH SPE Tasks for Fractionation of EPH Sample into Aliphatic and Aromatic Fractions

The details of each step are as follows:

- Initialization Step: Gilson Mobile SPE Racks are moved above the waste rack (Figure 3).
- Condition the cartridge with 5 mL acetone followed by an air push.
- Condition the cartridge with 6 mL methylene chloride (dichloromethane) followed by an air push.
- Condition the cartridge with 6 mL of hexane and allow the cartridge to stay moist (no air push).
- Load 1 mL of sample and 100 µL of fractionation surrogate onto the cartridge at a low flow rate. *Note: Silica cartridges must not be overloaded with excessive mass of hydrocarbons. Limit loading to 5 mg total hydrocarbon per gram of silica gel.*
- Move the Gilson Mobile SPE Rack over the collection tubes.
- Elute the Aliphatic Fraction with 2400 µL of hexane. Allow to drip into the collection tube (15 x 85 mm glass tube) by gravity. *Note: The amount of hexane used in this step is critical. Excessive use of hexane may cause elution of aromatics into the aliphatic fraction. Insufficient hexane will cause low recoveries of the aliphatic fraction. Adjust the amount of hexane if necessary based on your QC results.*
- Move the cartridges to the next set of collection tubes (Fractionate task) and elute the aromatic fraction with 4 mL of methylene chloride (dichloromethane). Allow to drip into the collection tube and then apply positive pressure to remove any excess solvent into the tube.
- Concentrate the two fractions using a Caliper TurboVap or equivalent evaporation system to a final volume of 1 mL. Be careful not to concentrate below 1 mL.
- The two fractions are then ready for analysis.

Figure 3. Gilson Mobile Rack

GC/ FID Analysis

GC/FID Analysis was performed on an Agilent 6890 GC (Dual ALS) with FID Detector. Separation was achieved using a Restek Rtx®-5 column (30 m x 0.25 mm, 0.5 µm). The carrier gas was helium at a flow rate of 1.5 mL/min. The injector temperature was 290°C and the injector detector temperature was 330°C.

A working calibration curve or calibration factor was verified each working day. A mid-level calibration standard was run after every 10 samples. The target compounds Naphthalene and 2-methylnapthalene were monitored in the Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) for breakthrough into the aliphatic fraction. If the concentration of either compound exceeded 5% of the total concentration (aromatic and aliphatic sum), fractionation was repeated.

Results

Table 2. MADEP EPH Fractionation Check Standard Results

Analyte	True Value (µg/mL)	STD Conc. (µg/mL)	% Recovery	Spike Limits
Napthalene	25.00	22.290	89	40–140
2-Methylnapthalene	25.00	22.529	90	40–140
Acenaphthylene	25.00	24.126	97	40–140
Acenaphthene	25.00	23.156	93	40–140
Fluorene	25.00	23.135	94	40–140
Phenanthrene	25.00	22.689	91	40–140
Anthracene	25.00	24.041	96	40–140
Fluoroanthene	25.00	22.650	91	40–140
Pyrene	25.00	22.873	91	40–140
Benzo(a)anthracene	25.00	23.470	94	40–140
Chrysene	25.00	24.218	97	40–140
Benzo(b)fluoranthene	25.00	24.157	97	40–140
Benzo(k)fluoranthene	25.00	22.468	90	40–140
Benzo(a)pyrene	25.00	21.509	86	40–140
Indeno(1,2,3-cd)pyrene	25.00	22.484	90	40–140
Dibenzo(a,h)anthracene	25.00	22.699	91	40–140
Benzo(g,h,i)perylene	25.00	22.121	88	40–140
C9	25.00	28.542	114	40–140
C10	25.00	26.110	104	40–140
C12	25.00	24.054	96	40–140
C14	25.00	23.863	95	40–140
C16	25.00	23.528	94	40–140
C18	25.00	22.858	91	40–140
C19	25.00	24.286	97	40–140
C20	25.00	24.364	97	40–140
C22	25.00	23.476	94	40–140
C24	25.00	22.567	90	40–140
C26	25.00	25.495	102	40–140
C28	25.00	24.191	97	40–140
C30	25.00	22.953	92	40–140
C36	25.00	26.394	106	40–140

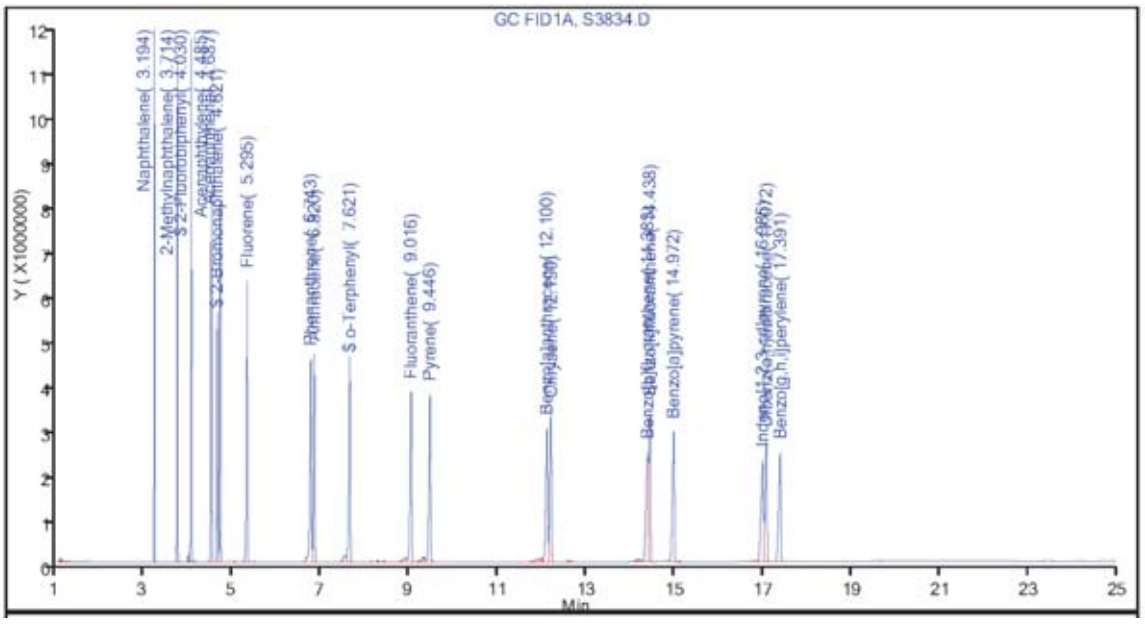

Figure 4. GC/FID Chromatogram of Aromatic Hydrocarbons after Automated Silica Gel Cartridge Fractionation of Water Extract Containing Fractionation Surrogate

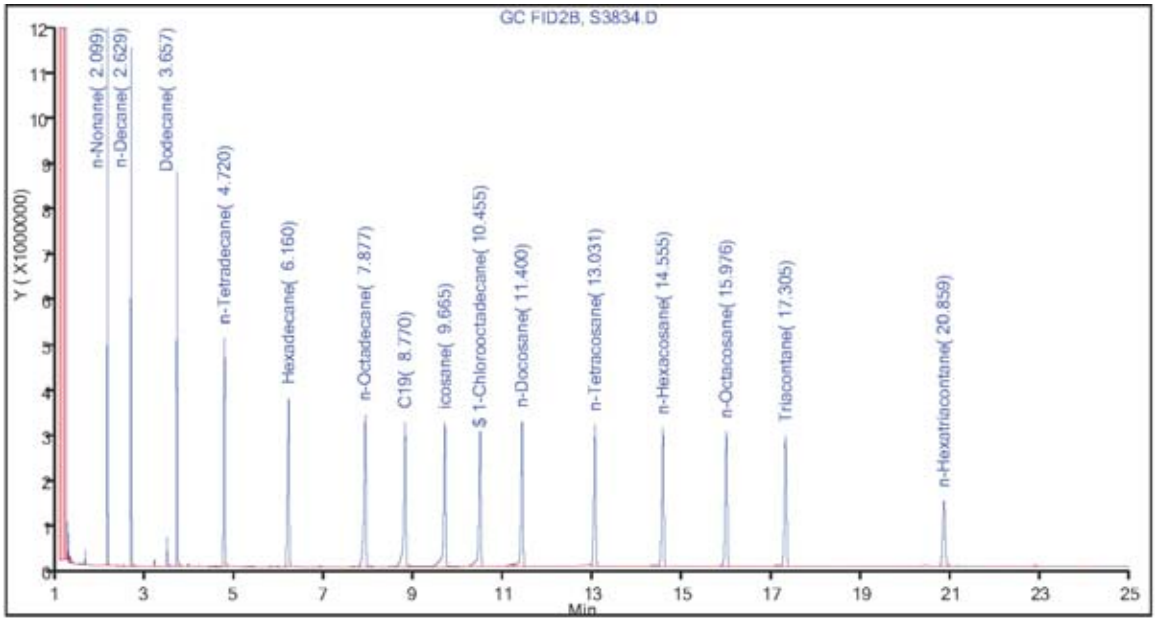

Figure 5. GC/FID Chromatogram of Aliphatic Hydrocarbons after Automated Silica Gel Fractionation of Water Extract Containing Fractionation Surrogate

Conclusion

This application note describes the conditions necessary to automate the fractionation of EPH into aliphatic and aromatic fractions using the Gilson GX-274 ASPEC System with Biotage ISOLUTE Silica Gel Cartridges. Recovery of all analytes was excellent. No aromatics were observed in the aliphatic fraction. Automation of the fractionation process improved day-to-day reproducibility and increased sample throughput compared to results obtained using the manual fractionation method. This automated method has now been fully validated in our laboratory. Automation of the EPH fractionation process has the additional benefits of reducing solvent usage, lowering the cost per test and allowing scientists to spend more time developing new methods for the analysis of compounds of interest in the environmental laboratory.

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