

# The Identification of Spilled Oil by the Pattern of Alkyl PAH

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## <Abstract>

In order to identify the origin and nature of the spilled oil in the potential source, we analyzed the pattern of alkyl PAH(Polynuclear Aromatic Hydrocarbons) in fuel standard and environmental samples. Alkyl PAH patterns are used for fuel-type identification in weathered environmental samples. Detection of alkyl PAH was achieved by operation GC/MS in the SIM mode. We chose ions of naphthalene(m/z 128), C1-naphthalene(m/z 142), C2-naphthalene(m/z 156), C3-naphthalene(m/z 170), C4-naphthalene(m/z 184) for the comparison of this pattern according to the type of fuel. We analyzed the pattern of alkyl PAH in neat gasoline, kerosene, diesel, and JP-8, and in groundwater samples which were collected in monitoring wells. The distribution map of alkyl-naphthalene shows different patterns among four different fuel types (gasoline, kerosene, diesel, and JP-8). Particularly, the distribution map of kerosene and JP-8 is found to be of value in identifying fuel type in that the difference is clear. Therefore distribution patterns of alkyl-PAH compounds provide another useful tool for fuel-type identification of petroleum fuels.

**key word** : alkyl PAH, spilled oil, alkyl-naphthalene, fuel-type identification

## 1. Introduction

The most samples received for identification will have undergone changes in composition, or weathering. The most immediate effect of weathering is the loss of lower compounds by evaporation. The nature and extent of this loss depends on the original composition of the spill and climatic conditions prevailing at the time. Thus, a gasoline spill on water is quite likely to have disappeared within 48hr, but cases have been known where this time scale has been doubled because of emulsion formation<sup>1)</sup>.

Other weathering processes such as biodegradation(the ultimate weathering process), oxidation, and

solution will also cause considerable changes in the composition of the oil, and the oil itself may act as a solvent for other pollutants and detergent emulsifiers which may be present<sup>2)</sup>.

Distribution patterns of PAH(polynuclear aromatic hydrocarbons) compounds provide another useful tool for monitoring environmental alteration of heavy-end petroleum fuels. Some of alkylated monoaromatic and PAH compounds of diesel of diesel fuel and Bunker C are among the least affected by weathering. The PAH parameters suggested in the extensive studies of Douglas et al.<sup>3)</sup>

The 1950s saw the initial major effort toward the development of methods to identify and measure polynuclear aromatic hydrocarbons. By the mid-1960s many papers had appeared on methods of analysis. Contributions came from laboratories of the United States, Canada, Australia, Europe, and Japan. In 1964, Sawicki[19] reviewed the analysis of PAHs based on a list of 244 references.

To confirm the source of the contamination, the type of fuel in the contaminated area should be identical to potential source of the contamination. The different pattern of PAH is depending on the type and the source of petroleum hydrocarbon. PAH and alkyl-PAH pattern are relatively stable components in petroleum. They are chemically stable and used frequently to identify fuel type of weathered or decomposed samples in environment.

Therefore this research is to identify the source of contamination by analyzing the pattern of alkyl PAH in fuel standard, and environmental sample.

## 2. Materials and methods

### 2.1 Chemicals and reagents

The methylene chloride used for this study was solvent used for analyzing residual agricultural chemical produced by Merck and the standard materials of alkyl PAH were

purchased from Aldrich or Sigma. Analytical grade of sodium sulfate( $\text{Na}_2\text{SO}_4$ , Kanto, Japan, for pesticide residue) were used as reagents. Water was purified in milli-Q(Millipore Corp., Milford, MA). Neat gasoline, kerosene, and diese samples were obtained from commercial gas station and JP-8 from L-oil Company. Weathered fuel were collected from monitoring well as free product found floating on top of the water. The fuel samples, After they arrived for the study, were extracted immediately.

### 2.2 Extraction procedure of free product and ground water

Take one milliliter of free product to the tube with a cap and dilute the sample with 10.0 mL of methylene chloride. Add 2.0 g of the anhydrous sodium sulfate and then shake well for about 2 minutes. Filter it through the disposable Pasteur pipette filled with 2 to 3 cm glass wool and put about 2 mL in the clean vial, then start measuring.

This method is a procedure for extracting organic materials contained in water samples to separate and concentrate them in the suitable form for measurement. Take an exact 200 mL of water sample using a cylinder and put it into a separatory funnel. Add 60 mL of methylene chloride and 50g of sodium chloride. Close the cap and vigorously shake the separatory funnel for 1 to 2 minutes while periodically venting the gas. Leave it for about 10 minutes to separate the organic layer from the water layer and then remove the organic layer using the Erlenmeyer flask. Repeat the extraction twice

more and solvents concentrate the extracted using the K-D concentrator. Connect the Kuderna-Danish (K-D) concentrator to 500 mL of evaporation flask using 10 mL concentrator tube and then let the extract pass the drying column filled with anhydrous sodium sulfate. Concentrate the extracted solvent in a water bath (30 ~ 40 C) using 20 to 30 mL of the methylene chloride in a way that part of the concentrator tube is sunk in the bath. Once the volume of the concentrated solution reaches to 1mL, remove the K-D concentrator and wipe the inside of the concentrator with 1 mL of the extracted solvent and combine it with the concentrated liquid.

### 2.3 Gas chromatography-mass spectrometry

GC/MS was used for the analysis of pattern of alkyl PAH. Secure patterns of purchased gasoline, kerosene, diesel, JP-8, and alkyl PAH. Compare these patterns of sample using GC-MS(SIM). A comparative analysis identifies the pattern of alkyl PAH of C0-naphthalene ~ C4-naphthalene.

All mass spectra were obtained with a Agilent 6890/5973 N instrument. The ion source was operated in the electron ionization mode (EI; 70 eV, 230°C). Full-scan mass spectra (m/z 40-800) were recorded for the identification of analytes at high concentration. GC separation of alkyl PAHs was made by non-polar stationary phase (DB-5). GC/MS selective ions of alkyl PAHs(m/z) are C0-naphthalene (128), C1- naphthalene (142), C2-naphthalene (156), C3-naphthalene (170), C4-naphthalene (184).

## 3. Results and discussion

PAH and alkyl-PAH pattern are relatively stable components in petroleum and show different pattern depending on the type and source of petroleum hydrocarbon. They are chemically stable and used frequently to identify fuel type of weathered or decomposed samples in environment. Especially, alkylnaphthalenes of Alkyl-PAH are the components that are least affected by weathering in kerosene. Therefore, their distribution map was used in identifying fuel type in this study. Fig. 1 presents the distribution map of alkyl-naphthalene of four different fuel types (gasoline, kerosene, diesel, and diesel). It represents mass chromatogram of naphthalene (128), C1-naphthalene (142), C2-naphthalene (156), C3-naphthalene (170) and C4-naphthalene (184). The preceding five peaks of these peaks are the peaks of n-C9-, n-C10-, n-C11-, n-C12-, n-C13- alkane in order. The distribution map of alkyl-naphthalene including these peaks shows different patterns according to fuel type. Particularly, the distribution map of kerosene and JP-8 is found to be of value in identifying fuel type in that the difference is clear.

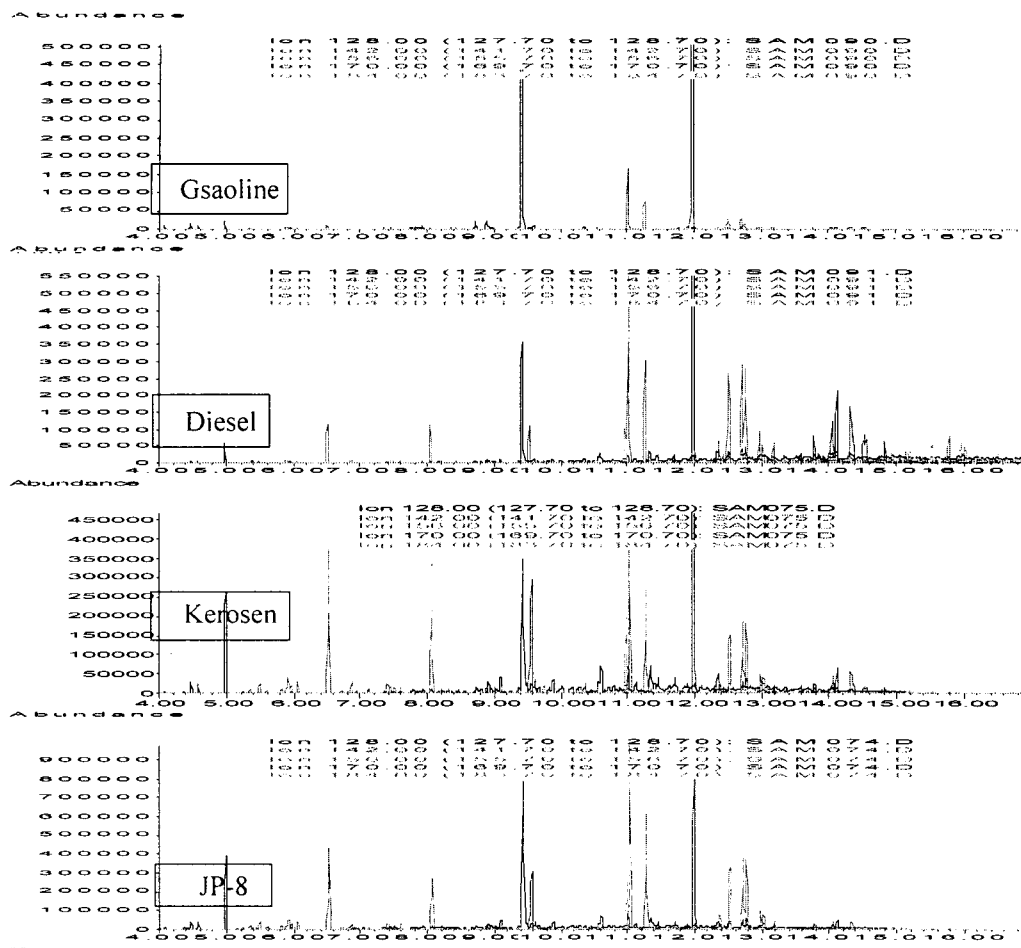


Fig. 1. Alkyl-PAH patterns of four different fuel type(Gasoline, Diesel, Kerosene, JP-8)

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