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The Source Identification of Spilled Oil by Pristane/Phytane Ratio

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요 약 문

잠재오염원에서 누출된 유류의 기원을 확인하기 위해서 표준연료와 환경시료중의 유류 구성성분의 농도를 분석하였다. pristane/phytane의 비는 환경시료 중 같은 휘발성을 가지고 있기 때문에 실질적으로 변하지 않는다. 이것은 미생물분해와 풍화의 영향을 평가하고 유류의 오염원을 확인하는데 유용하였다. L과 S 주유소에서 백등유, 보일러등유, JP-8, 경유의 pristane/phytane 비를 측정하였다. L-백등유와 JP-8에서 pristane/phytane 비는 각각 3.10±0.03, 1.77±0.01였으며, 유류와 물을 분배시킨 후 물층에서 pristane/phytane 비는 백등유 2.97±0.02, JP-8 1.65±0.02였다. pristane/phytane 비는 백등유와 JP-8을 구분하는 유효하였으며, 또한 관측정에서 수집된 자유상유류와 지하수시료에서 유종을 확인하는데 유용하였다.

ABSTRACT

In order to identify the origin and nature of the spilled oil in the potential source, we analyzed the concentrations of specific fuel constituents in fuel standard and environmental samples. The ratios of pristane/phytane are virtually unaltered because these compounds have the same bolatility in environmental samples. These were useful to identify the source of the fuel oil and to assess the effect of microbial degradation and weathering of the fuel oil. We analyzed the ratios of pristane/phytane in neat white kerosene, boiler kerosene, JP-8 and diesel products from L and S gas station. The ratios of pristane/phytane in L-white kerosene and JP-8 was 3.10 ±0.03 and 1.77 ±0.01, respectively. Otherwise, the ratios of pristnae/phytane in water phase after distribution of fuel oil and water was 2.97 ±0.02 in case of white kerosene and 1.65 ±0.02 in case of JP-8. It is apparent from the results that the ratios of pristane/phytane were as product-specific, especially between kerosene and JP-8, and therefore, can also be used for fuel type identification in free products and groundwater samples which were collected in monitoring wells

Key words : Fuel oil, Pristane, Phytane, Kerosene, JP-8, Fuel type identification

1. Introduction

Soil and groundwater contamination caused by accidental spill and leak of fuel oil has been escalating in line with the industrialization and the growing consumption of energy. To confirm the source of the contamination, the type of fuel in the contaminated area should be identical to potential source of the contamination. A simple pattern analysis of hydrocarbon cannot provide the answer. Fuel is a quite complicated compound ranging a simple straight chain-type saturated hydrocarbon (n-alkane), unsaturated hydrocarbon and aromatic hydrocarbon, etc. Once exposed to the environment, oil undergoes various chemical processes including volatilization, dissolution, microbial or chemical decomposition, which drastically transforms the saturated hydrocarbon[1,2,3]. This makes it impossible to accurately identify the type of Fuel with the simple hydrocarbon pattern analysis. Hydrocarbon molecules are composed of one or more carbon atoms joined to one another and also to hydrogen atoms (*alkanes, also called paraffins*). The carbon atoms may form a straightchain (*n-alkane*), a branched-chain (*iso-alkane*), or a ring (*cycloalkanes, cycloparaffins* or *naphthenes*) structure[4]. Middle distillate products generally includes mineral spirits and stoddard solvent, kerosene,

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most of the jet fuels, diesel, and light fuel oils. Because of the extreme complexity of the composition of petroleum-related products, no single analytical method can be used to identify all of its important components in environmental samples. Moreover, because petroleum is a labile mixture, the composition of a product released into the environment begins to change almost immediately because of numerous biochemical and physical processes.

It very difficult to identify the source of contamination, because most of oil refineries in Korea use a same quality crude oil. But it is believed that a very thorough and detailed analysis of the chemical features of the oil could identify the subtle difference between oil types. This will enable us to identify the source of contamination. Most oil goes through volatilization, dissolution and microbial or photochemical decomposition processes but the compounds which were not transformed can be utilized as a very important marker[5].

Therefore development of the most reliable and accurate analytical method is essential. Required is a method that allows the most reliable and accurate analysis. Especially, the pattern analysis of the difficult-to-decompose contained in the oil can be used as a very useful index to distinguish the oil type and analysis of pristane/phytane ratio can provide a clue to determine the source of contamination[6].

Therefore this research is to identify the source of contamination by analyzing pristane/phytane ratio in fuel standard, especially between kerosene and JP-8, and environmental sample.

2. Experimental

2.1 Chemicals and reagents

Heptacosane ($C_{17}H_{36}$), Octacosane ($C_{18}H_{38}$), Pristane ($C_{19}H_{40}$), and Phytane ($C_{20}H_{42}$) were purchased from Sigma (USA, special reagents). Analytical grade of sodium sulfate (Na_2SO_4, Kanto, Japan, for pesticide residue) were used as reagents, and methylene chloride (CH_2Cl_2, Kanto, Japan, for pesticide residue) was used as solvents. Water was purified in milli-Q (Millipore Corp., Milford, MA). neat gasoline, white kerosene, boiler kerosene, and diesel 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 groundwater

2.2.1 Extraction procedure of free product

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.

2.2.2 Extraction procedure of groundwater

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. 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 1 mL, 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

All the GC/MS conditions are displayed in Table 1. The ion source was operated in the electron ionization mode (EI; 70 eV, 230°C)[7,8]. Confirmation of trace chemicals was completed by MS characteristic ions (SIM, m/z 85) and GC-retention times matches to the known standard compounds. GC separation of pristane and phytane was made by non-polar stationary phase (DB-5).

Table 1. GC/MS Conditions for the determination of Pristane/Phytane ratio

Parameter	Condition
GC	Agilent 6890 instrument
Column	HP-5ms (30 m×0.25 mm I.D×0.25 μm F.T)
Carrier gas	He at 2.0 mL/min
Oven Temp.	40°C (5°C/min)→100°C (8°C/min) →275°C (5 min)
Injector Temp.	200°C
Transfer Temp.	290°C
Selected Ion	SIM mode 85m/z

2.4 Calibration and quantification

Dissolve standard materials of pristane, phytane (restek, 2000 μg/ml) in methylene chloride. Dilute the standard solution with methylene chloride to make a mixed standard solution of a certain concentration (0.01 to 2 μg/ml) in 5 steps. Store the undiluted standard solution and mixed standard solution in a dark area whose temperature is −5°C or lower.

3. Results and discussion

3.1 Pristane/phytane ratio of fuel standard sample

Unknown petroleum hydrocarbon has specific fingerprint depending on its fuel type, but environmentally contaminated oil changes its pattern by weathering, distribution of the phases and evaporation. However, branched hydrocarbon type (isoprenoid) is important in some respect as following because it is not greatly affected by weathering. It is helpful to predict the degree of microbial degradation by measuring changes of components of n-hydrocarbon type and isoprenaline of oil. Especially, in this case, it helps to predict the degree of microbial degradation of oil using the ratio between n-C_{17}/pristane and n- C_{18}/phytane. The reason is that while n-C_{17} and n-C_{18} are vulnerable to environmental decomposition by microorganism, pristane and phytane are not resolved easily and their ratio gets smaller as degree of environmental weathering by microorganism gets bigger since n- C_{17} and pristane, and n-C_{18} and phytane have similar volatility. This indicator is used as an indicator material to identify the degree of microbial degradation.

Chromatograms of $C_{17}H_{36}$, pristane, $C_{18}H_{38}$ and phytane in JP-8 are presented in Fig. 1. All of them showed symmetry and well separated peaks.

Homogeneity of oils can be traced using the ratio between pristane and phytane of oil components. This is due to the fact that pristane and phytane, of branched saturate isoprenoids, are not decomposed easily by microorganism and its ratio remains the same environmentally for a long time.

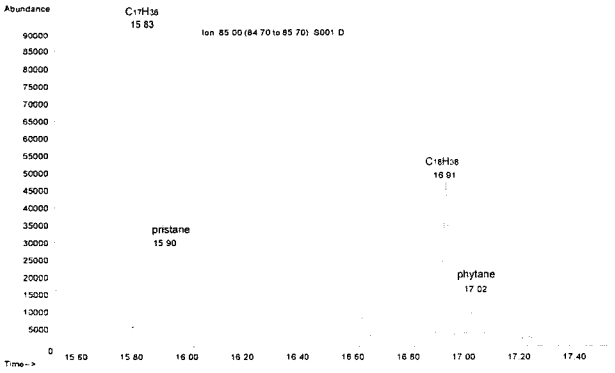

Fig. 1. Chromatograms of $C_{17}H_{36}$, pristane, $C_{18}H_{38}$ and phytane in JP-8.

In this study, we obtained materials of m/z 85 GC-MS (SIM) by extracting fuel standard samples and the result is shown as follows Fig. 2. And we analyzed them with white kerosene, JP-8 (aviation turbine fuel), boiler kerosene, and diesel fuel standard sample obtained from L and S gas station.

GC/MS (SIM) material of m/z 85 plays an important role in estimating its fuel type. Especially, it is useful in identifying very small amount of kerosene that is mixed with a quantity of gasoline.

We measured the ratio of pristane/phytane of oil components and found that the ratio of L-white kerosene was 3.10±0.03, and that of S-white kerosene was 3.57±0.02, all of which double the value of JP-8 (1.77±0.01). It was useful in distinguishing between similar two fuel types in the pattern of Total Petroleum Hydrocarbons (TPH). Pristane/phytane ratio of L-boiler kerosene with great difference between JP-8 and TPH pattern was 1.31±0.03, SK-boiler kerosene was 1.55±0.02 and diesel was 0.81±0.02.

According to the ratio of pristane/phytane measured after distributing oil component into water layer to measure the ratio of pristane/phytane of groundwater, it was found that the ratio of L-white kerosene of similar pattern of JP-8 and TPH was 2.97±0.02, that of S-kerosene was 3.43±0.03, while JP-8 presented a large differences showing the value 1.65±0.02. And the ratio of L-boiler kerosene with large difference of pattern of JP-8 and TPH was 1.30±0.02 and that of S-boiler kerosene was 1.27±0.02.

The result of significance test between fuel and water-fuel standard are displayed in Table 2. All P-value between fuel and water-fuel standard was below 0.01

3.2 Pristane/phytane ratio of environment samples

In this study, we obtained materials of m/z 85 GC-MS

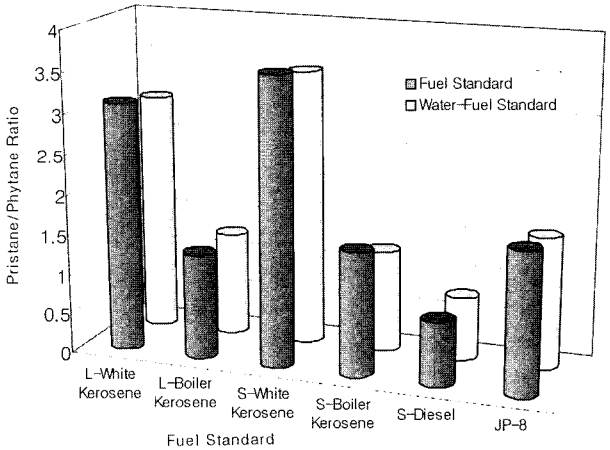

Fig. 2. Pristane/Phytane ratios of fuel standard and water-fuel standard. Water-fuel standards were distributed oil component into water layer.

Table 2. Results of significance test between fuel and water-fuel standard (n=3)

Index \ Fuel Type	L-White Kerosene Pristnae/Phytane Ratio	S-White Kerosene Pristane/Phytane Ratio	JP-8 Pristane/Phytane Ratio
Fuel Standard (Mean±SD)	3.10±0.03	3.57±0.02	1.77±0.01
Water-Fuel Standard (Mean±SD)	2.97±0.02	3.43±0.03	1.65±0.02
Result of t-test	7.65	7.37	11.70
P-value	P<0.01	P<0.01	P<0.01

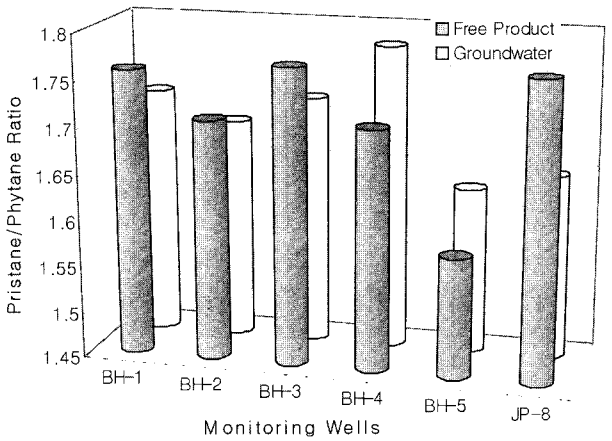

Fig. 3. Pristane/phytane ratios of free products and groundwater samples in monitoring wells.

(SIM) by extracting free products and groundwater samples which were collected in monitoring wells and the result is shown as follows Fig. 3.

We compared and analyzed them with white kerosene, boiler kerosene, JP-8, and diesel control standard sample neighboring L gas station and S gas station around oil contamination accident area. As for the analytical result of free product samples, the ratio of pristane/phytane in most of the sample identified as kerosene (or JP-8) in TPH pattern analysis was 1.58~1.77. It was very similar to the ratio of JP-8. It was found that the ratio of the groundwater samples was 1.63~1.78, which was, very similar to that of JP-8.

Therefore, the ratios of pristane/phytane can also be used for fuel type identification in free products and groundwater samples which were collected in monitoring wells.

4. Conclusions

The ratios of pristane/phytane are virtually unaltered because these compounds have about the same volatility. These are useful to identify the source of the oil and to assess the effect of microbial degradation and weathering of the oil.

We analyzed the ratios of pristane/phytane in white kerosene, JP-8, boiler kerosene, and diesel fuel standard. The ratios of pristane/phytane in white kerosene and JP-8 ranged with 3.10±0.03 and 1.77±0.01, respectively. Otherwise, the ratios of pristane/phytane in water phase after distribution of oil and water ranged with 2.97±0.02 in case of white kerosene and 1.65±0.02 in case of JP-8. Those of pristane/phytane in free product samples in monitoring wells ranged with 1.58~1.77. Otherwise, those of pristane/phytane in groundwater samples in monitoring wells ranged with 1.63~1.78.

References

1. Atlas, R. M. "Microbial degradation of petroleum hydrocarbons: an environmental perspective", *Microbiological Review*, **45**(1), pp. 180-209 (1981).
2. Bray, E. E., and Evans, E. D. "Distribution of n-paraffins as a clue to recognition of source beds", *Geochimica Cosmochimica Acta*, **22**, pp. 2-15 (1961).
3. Baughman, G. L., and Paris, D. F. "Microbial bioconcentration of organic pollutants from aquatic systems - a critical review", In CRC Critical Reviews in Microbiology, Junuary, pp. 205-228(1981).
4. Hoffman, H. L., and McKetta, J. J., Petroleum Processing Handbook, Marcel Dekker, Inc. NY, pp. 82-101(1992).
5. Peters, K. E., and Moldowan, J. M., The Biomarker Guide, Prentice-Hall, Inc. *Englewood Cliffs*, NJ, pp. 363 (1993).
6. Douglas, G. S., Bence, A. E., Prince, R.C., McMillen, S. J., and Butler, E. L. "Environmental stability of selected petroleum hydrocarbon source and weathering ratios", *Environmental Science and Technology*, **20**(7), pp. 2332-2339 (1996).
7. Kaplan, I. R., Galperin, Y., Alimi, H., Lee, R. P. and Lu, S. T. "Patterns of chemical changes during environmental alteration of hydrocarbon fuels", *Groundwater Monitoring and Remediation*, **16**(4), pp. 113-124 (1996).
8. Kaplan, I. R. and Galperin, Y. "Application of alkylcyclohexane distribution pattern recognition for hydrocarbon fuels identification in environmental samples", *Proceedings of the 11th Annual conference on contaminated soil, October, 21-24, Amherst, Massachusetts (1996).*