



Discriminatory Analysis of Discharged Gas and Heavy Oils in the Sea

Masato Taki^{1,*}; Akira Yoshida¹; Kei Machigashira¹; Masaki Sakon¹; Masatoshi Nagai²

¹Coast Guard Research Center, Japan Coast Guard, 1156, Tachikawa-city, Tokyo 190-0015, Japan

²Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24, Nakamachi, Koganei-shi, Tokyo 184-8588, Japan

*Corresponding author.

Email: masato-taki@jcom.home.ne.jp

Received 7 August 2011; accepted 14 September 2011.

Abstract

Gas and heavy oils discharged into the sea were discriminated using gas chromatography-mass spectrometry (GC-MS), gas chromatography (GC-FID) and infrared spectroscopy (FT-IR). The GC-MS focused on the determination of the biomarkers, such as hopanes, norhopanes and triaromatic steranes, which were detected from heavy oil, but were hardly observed from gas oil. The discriminative analysis using GC-FID of the methylnaphthalenes showed a discrimination with a ratio of ((2-methylnaphthalene)+(1-methylnaphthalene))/tridecane. The ratios for the gas oils were less than 1.0, but those for the heavy oils were 1.0 or higher. These oils were distinguished in comparison to the FT-IR data from three peaks at 811, 742 and 723 cm^{-1} which were assigned to the CH bending modes for 2 and 4 hydrogens and a methylene framework, respectively. The order for the heavy oil was $723 < 742 < 811 \text{ cm}^{-1}$, while that for the gas oil was $742 < 811 < 723 \text{ cm}^{-1}$. Moreover, the absorption intensity at 1603 cm^{-1} for the heavy oil was higher than that for the gas oil. An absorption at 475 cm^{-1} (out-of-plane ring vibration) was also observed for the heavy oil, but not for the gas oil. In combination of the GC results with the FT-IR, 2-methylnaphthalene and 1-methylnaphthalene were contained in greater amounts in the heavy oil than in the gas oil, which were derived from the light cycle oil. Thus, the heavy oils discharged from ships and drifted on the seashore were discriminated from the original heavy oils and the gas oils.

Key words: Heavy oil, Gas oil, Identification,

Methylnaphthalene, Hopane

Masato Taki, Akira Yoshida, Kei Machigashira, Masaki Sakon Masatoshi Nagai (2011). Discriminatory Analysis of Discharged Gas and Heavy Oils in the Sea. *Advances in Petroleum Exploration and Development*, 2(1), 19-24. Available from: URL: <http://www.cscanada.net/index.php/aped/article/view/10.3968/j.aped.1925543820110201.592> DOI: <http://dx.doi.org/10.3968/10.3968/j.aped.1925543820110201.592>

INTRODUCTION

Recently, oils discharged from an offshore will have caused marine pollution and heavy damage to aquatic life by accidents during the crude oil drilling and the grounding of supertankers during transportation. In order to identify the sources of such pollution, urgent analytical methods needed to be established; (1) the discrimination among the types of gas, heavy and crude oils, and (2) the identification of each oil. Discrimination of the gas and heavy oils using GC with a flame photometric detector (GC-FPD) and GC-MS has focused on the sulfur compounds^[1,2]. However, since the sulfur in gas and heavy oils has recently been reduced by the environmental reference concentration, the sulfur compounds are presently difficult to analyze because of their low amounts in the oils. Thus an alternative index is needed for the discrimination. In a previous paper^[3], 41 types of crude oils, such as from the Middle East, South East Asia, Gabon, Russia and Mexico and their spilled oils were specified for the country or area of origin based on biomarkers. This discriminative analysis was performed using a combination of analyses for biomarkers such as hopanes, norhopanes and oleananes as well as nickel and vanadium, and the analysis of sulfur in the crude oil. A large quantity of 17α -21 β (H)-norhopane (C_{29} hopane) is included in crude oil from the Middle East and originated from bacteria in the evaporite and carbonate rocks from before the Cretaceous period. 17α -21 β (H)-

hopane (C_{30} hopane) is considered to come from bacteria in mudstone^[4] since the maturing of oil in sedimentary environments causes the transformation of monoaromatic sterane to triaromatic sterane ($m/z=231$)^[5] which is used as an index of oil maturity in the oil exploration field. To analyze the gas and heavy oils discharged into the sea, the triaromatic steranes in addition to hopanes and norhopanes were selected as the discriminative indices, which act as biomarkers in the heavy oil. The gas and heavy oils in the sea were discriminated by focusing on the analysis of hopanes, norhopanes and triaromatic steranes using GC-MS. Moreover, 2-methylnaphthalene (2-MN) and 1-methylnaphthalene (1-MN) were more significantly observed in the heavy oil than in the gas oil, which were observed near the tridecane peak at the retention time using the CBP1 capillary column of GC-FID. The analysis of these three compounds can discriminate the heavy oil from the gas oil.

FT-IR spectroscopy is very useful in determining the structure of organic compounds with functional groups contained in the gas and heavy oils in order to determine what creates the difference between them in about one minute. Although a number of conventional studies has described discriminative analysis of crude oil^[6,7] using FT-IR at 1600 cm^{-1} , no analysis method for the discrimination between the gas and heavy oils has been reported. The FT-IR spectra at 2955 cm^{-1} (k), 2925 cm^{-1} (l), 2854 cm^{-1} (m), 1462 cm^{-1} (o) and 1377 cm^{-1} (p) in the gas and heavy oils are strongly and clearly observed, but these wavenumbers of the gas oil are only slightly distinguished from those of the heavy oil. Therefore, the difference between the gas and heavy oils was studied on the basis of the absorption at 1603 cm^{-1} (quadrant stretch), 811 cm^{-1} (deformation vibration (2 adjacent hydrogen)), 742 cm^{-1} (deformation vibration (4 adjacent hydrogen)), 723 cm^{-1} (deformation vibration) and 475 cm^{-1} (out-of-plane ring vibration). The latter four spectra are assigned to the CH bending modes for 2 and 4 hydrogens and a methylene framework. The gas and heavy oils were classified from the combination of the FT-IR with GC-FID. In this study, the gas and heavy oils were discriminated on the basis of the biomarkers by GC-MS and the specific spectra derived from methylnaphthalene by FT-IR and GC-FID.

1. EXPERIMENTAL SECTION

1.1 Lubricants and Reagents

Ten kinds of gas oils (SN-G, EX-G, TZ-G, MI-G, SS-G, TY-G, CO-G, IK-G, JN-G, KS-G) and 10 kinds of heavy oils (SN-H, EX-H, TZ-H, MI-H, SS-H, TY-H, CO-H, IK-H, JN-H, KS-H) were obtained from 10 filling stations at the oil refinery companies in Japan. A light cycle oil (LCO) was procured from a major domestic oil manufacturer in Japan as well. Gas and heavy oils sampled from the sea and those sampled from ships were

used. The heavy oil was a sample exposed to the sea for one and a half hours in 2011. The authentic standards of 18α -22, 29, 30-trisnorneohopane(Ts) (a), 17α -22, 29, 30-trisnorhopane(Tm) (b), 17α -21 β (H)-norhopane(C_{29} hopane) (c), 17α -21 β (H)-hopane (C_{30} hopane) (d), C_{26} triaromatic sterane (e), C_{28} triaromatic sterane (20S)(f), C_{27} triaromatic sterane (g) and C_{28} triaromatic sterane (20R) (h) were purchased as a Hopane and Triaromatic Sterane Kits from Chiron, Norway. The solvents such as hexane, 1-methylnaphthalene(1-MN) (i), 2-methylnaphthalene(2-MN) (j), tridecane (C_{13}) and sodium sulfate (anhydrous) were purchased from Wako Pure Chemical, Ltd. (Tokyo, Japan). The KBr cell was purchased from JASCO, Ltd. (Tokyo, Japan).

1.2 Preparation and Analysis of GC-MS and GC-FID

The gas and heavy oils were analyzed using Agilent Technologies equipment (Models HP5972 and HP5890) along with a J&W Scientific Durabond fused-silica capillary DB-1 column having an inner diameter (id) of 0.25 mm, a film thickness of 0.25 μm , and a length of 60 m with helium as the carrier gas (1.1 mL/min). The GC-MS operating conditions in the electron impact (EI) mode included an ionization potential of 70 eV with the ion source at 180 °C and the electron multiplier voltage at $\sim 1.2\text{ kV}$. The sample (1 μL) was injected into the injection port maintained at 320 °C in the split mode (1:50) and splitless mode. The column temperature was increased from 35 to 300 °C at the rate of 6 °C/min. The scan and selected-ion monitoring methods were applied after a delay of 7 min, and the hopanes and norhopanes were quantified at $m/z = 191$, and the triaromatic steranes were quantified at $m/z = 231$. The hopanes were analyzed by monitoring at $m/z = 191$. It is required to first confirm whether or not the hopanes were eluted from the inside of the column by the GC-MS scan method. The peaks were identified by comparison of their retention times to those for the standards and their mass spectra. The gas and heavy oils were analyzed using GC-17A Shimadzu equipment along with a fused-silica capillary CBP1 column having an inner diameter (id) of 0.53 mm, a film thickness of 1.0 μm , and a length of 25 m with a helium carrier gas (8 mL/min). The sample (0.5 μL) was injected into the injection port maintained at 320 °C. The column temperature was increased from 80 to 300 °C at the rate of 6 °C/min. Each sample (1.00 g) was dissolved in 20 mL of hexane and then separated at 7000 rpm for 10 min using a centrifugal separator. The same separation procedure for the hexane-soluble material and insoluble residue in the oils was used instead of the method of extraction and fractionation.

1.3 Preparation and Analysis of FT-IR

The FT-IR spectra were measured by using JASCO equipment (Model FT/IR-410). The FT-IR operating conditions were as follows: permeation mode and

attenuated total reflection (ATR) mode, measurement range; 4000-400 cm^{-1} (ATR; 4000-650 cm^{-1}), detector; triglycine sulfate, resolution; 4 cm^{-1} , accumulated number; 64. An FT-IR microscope equipped with an ATR accessory (single reflection mode) utilizing a diamond crystal (JASCO, Ltd. Tokyo, Japan) was used.

2. RESULTS AND DISCUSSION

2.1 Analysis of Heavy Oil Sampled from the Sea

The heavy oils sampled from ships and drifting in the sea were determined using GC-MS. Figure 1 shows the chromatograms from a scan analysis of a heavy oil sampled from (A1) a ship and (A2) the sea. The peaks for heptane to heptacosane were observed in the heavy oil sampled from the ship. The higher peaks are due to tetradecane and pentadecane. The heavy oil sampled from the sea did not contain the compounds with boiling points lower than tetradecane, while the heavy oil from the ship did. This is because the heavy oil sampled from the sea was more easily evaporated than that from the ship. Furthermore, the peak intensity of the higher carbon numbers of the alkane compounds in the heavy oil had decreased. This tendency of the intensity decrease has proven to be difficult to discriminatively analyze the weathered heavy oil using the alkane as an index.

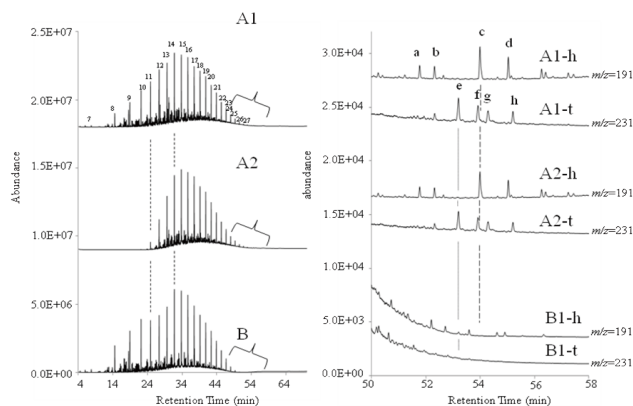


Figure 1
Total Ion Chromatogram of the Heavy Oils (A1, A2) and Gas Oil (B) m/z 191 and m/z 231 Mass chromatograms of the heavy oils (A1-h, A1-t, A2-h and A2-t). The notations (a-h) are illustrated in Figure 2. Total ion chromatogram of the gas oils (B1). m/z 191 and m/z 231 Mass chromatograms of the gas oils (B1-h, B1-t)

The biomarkers, such as hopanes, norhopanes and triaromatic steranes, were useful in discriminating the crude oil^[3,5] and lubricants^[8], but little was detected

from the gas oil as shown in Figure 1B. As a result, the determination of hopanes and triaromatic steranes can significantly discriminate the heavy oil from the gas oil. Figure 2 shows the structural formulas (e-g) for the triaromatic steranes. The triaromatic steranes correspond to (C_{26} - C_{28}) in Figure 1. Since the triaromatic steranes were clearly observed with no interference from other substances, they were used as the discriminative indices. Figure 2 shows the structural formulas (a-d) for the hopanes and norhopanes. The chromatograms for the hopanes of $m/z = 191$ and 231 from the heavy oil sampled from a ship and the sea are shown in Figure 1 (A1-h, A1-t, A2-h and A2-t). The hopanes correspond to the arrows (C_{25} - C_{27}) in Figure 1A. This result shows that the sea heavy oil was different from the ship sample. The peaks of a, b, c and d for the ship sample were slightly higher than those for the sea sample. The peak of 18 α -22,29,30-trisnorhopane (Ts) (a) is slightly higher than those of 17 α -22,29,30-trisnorhopane (Tm) (b) and 17 α -21 β (H)-norhopane (C_{29} hopane) (c) and than that of 17 α -21 β (H)-hopane (C_{30} hopane) (d). (a) and (b) are less affected by the biodegradation. The former is more stable than b, which is extensively found in crude oil derived from green algae or bacteria^[5,9] from the northern Middle East. (a) is used as an index of the oil maturity in the oil exploration field^[5,10]. Furthermore, the peaks of the triaromatic steranes (e, f, g and h) in the ship sample were higher than those in the sea sample with a behavior similar to the highest peaks of e. Consequently, the GC-MS analysis of the hopanes and triaromatic steranes differentiated the heavy oil sampled from a ship from that sampled from the sea.

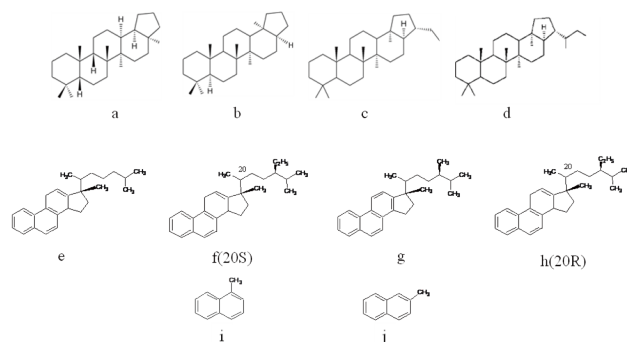


Figure 2
Structures of the Hopane Compounds: a, 18 α -22, 29, 30-trisnorhopane; b, 17 α -22, 29, 30-trisnorhopane; c, 17 α -21 β (H)-norhopane (C_{29} hopane); d, 17 α -21 β (H)-hopane (C_{30} hopane); e, triaromatic sterane(C_{26}); f, h, triaromatic sterane(C_{28}); g, triaromatic sterane(C_{27}); i, 1-methylnaphthalene; j, 2-methylnaphthalene

2.2 Analysis for Discrimination Between Gas and Heavy Oils from LCO

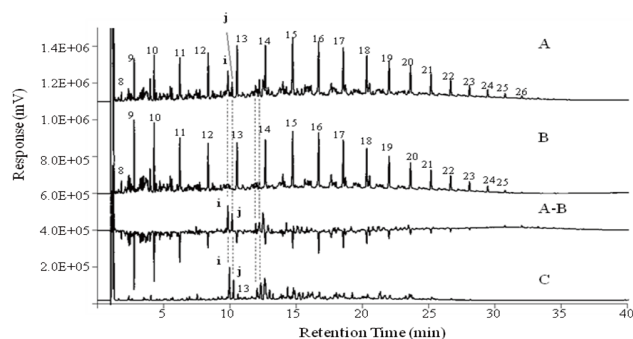


Figure 3
GC-FID of Heavy Oil (A), Gas Oil (B), Difference Chromatograms of Heavy Oil and Gas Oil (A-B), and of Light Cycle Oil (C)

The GC-FID chromatograms of the heavy and gas oils are shown in Figure 3. The peaks were identified using the GC-MS in parallel. The chromatogram for the heavy oil (A) showed a peak from octane to hexacosane with the highest peak for pentadecane. The chromatogram for the gas oil (B) showed a peak from octane to pentacosane with the highest peak for nonane. The alkanes present in the gas and heavy oils showed similar behavior. However, the peaks of 2-MN (i) (a retention time of 9.8

min) and 1-MN (j) (10.2 min) were observed only in the chromatogram for the heavy oil (A), while the peaks were hardly observed in the gas oil (B). The subtraction of the peaks of chromatogram A from those of B showed that the remaining and downward peaks were caused by the size of the alkane peaks of 2-MN and 1-MN. Thus, the gas and heavy oils showed differences in the size of each alkane peak as well as in 2-MN and 1-MN. Table 1 shows the results for 2-MN, 1-MN and the nearest peaks of 2-MN, 1-MN and C_{13} in the various commercial gas and heavy oils. It can be seen that both the gas and heavy oils had a higher concentration of 2-MN than that of 1-MN. The gas and heavy oils could be clearly discriminated by the ratio of $((2\text{-MN}) + (1\text{-MN}))/C_{13}$. The values for the gas oils were less than 1.0, whereas those for the heavy oils were 1.0 or higher. Moreover, LCO contains a corresponding boiling fraction produced by a fluid catalytic cracking (FCC) unit and is characteristic of more aromatic compounds than the straight diesel oil. The GC-FID results for this type of oil are shown in Figure 3C. The peaks of i and j in the chromatogram were observed for LCO as well as that subtracted from the heavy oil (A-B). 2-MN had a higher peak than 1-MN and the ratio between 2-MN and 1-MN was the same.

Table 1
The Concentrations of 2-Methylnaphthalene, 1-Methylnaphthalene, Tridecane and Ratio of $((2\text{-Methylnaphthalene}) + (1\text{-Methylnaphthalene}))/\text{Tridecane}$ in the Heavy and Gas Oils.

	2-MN (mg/g)	1-MN(mg/g)	C_{13} (mg/g)	$((2\text{-MN})+(1\text{-MN}))/C_{13}$	q/r	s/r	q/s	a/b	c/d	e/f
Gas Oil										
SN-G	4.9	3.0	14	0.55						
EX-G	8.1	4.2	17	0.72						
TZ-G	2.8	1.6	19	0.23						
MI-G	3.8	2.0	14	0.40						
SS-G	1.3	1.3	15	0.17	1.6	3.6	0.4			
TY-G	3.7	1.9	15	0.38						
CO-G	2.6	1.6	15	0.28						
IK-G	2.5	1.5	17	0.24						
JN-G	4.6	2.9	15	0.50						
KS-G	4.2	2.7	15	0.45						
Heavy Oil										
SN-H	8.3	4.8	7.1	1.8				0.98	1.89	1.78
EX-H	8.2	4.6	6.7	1.9				1.06	1.89	1.79
TZ-H	7.9	4.5	10	1.2				1.11	1.89	1.73
MI-H	11	6.4	6.1	2.9				1.12	1.88	1.75
SS-H	8.4	4.7	4.7	2.8	1.4	0.4	3.3	1.13	1.98	1.93
TY-H	11	5.9	7.3	2.3				1.13	1.88	1.75
CO-H	9.6	5.2	6.2	2.4				1.11	1.54	2.63
IK-H	7.9	4.2	7.5	1.6				0.96	1.72	2.13
JN-H	8.0	4.3	6.4	1.9				1.05	1.84	1.61
KS-H	9.7	5.4	10	1.5				1.79	1.90	1.60

2.3 Analysis for Discrimination Between Gas and Heavy Oils Using FT-IR

FT-IR is easier to use than GC-FID due to its extremely short measurement time and its measurement performance of a variety of compounds in oils ranging from low to high molecular weights. It is also possible to perform the FT-IR measurement using extremely small samples by

adopting ATR. For these reasons, FT-IR is useful for the determination of the different oil types. The FT-IR spectra of the heavy oil (upper stage A) and the gas oil (lower stage B) are shown in Figures 4A and 4B. The absorption at 2955 cm^{-1} is assigned to the asymmetric stretch; CH_3 (k), at 2925 cm^{-1} to the asymmetric stretch; CH_2 (l), at 2854 cm^{-1} to the symmetric stretch; CH_3 (m), at 1462 cm^{-1} to the

asymmetric deformation; CH₃ to the deformation; CH₂ (o), and at 1377 cm⁻¹ to the symmetric deformation; CH₃ (p). The absorption ratio at 1603 cm⁻¹ (quadrant stretch) (n) to that at 1462 cm⁻¹ is almost three times higher in the heavy oil than in the gas oil. Except for this absorption, however, the peaks ranging from 4000 to 1000 cm⁻¹ showed similar intensity levels in both oils. Based on these results, the compounds derived from the methyl and methylene groups were not differentiated, but the compounds from the aromatic ones allowed recognition of the difference between the gas oil and the heavy oil.

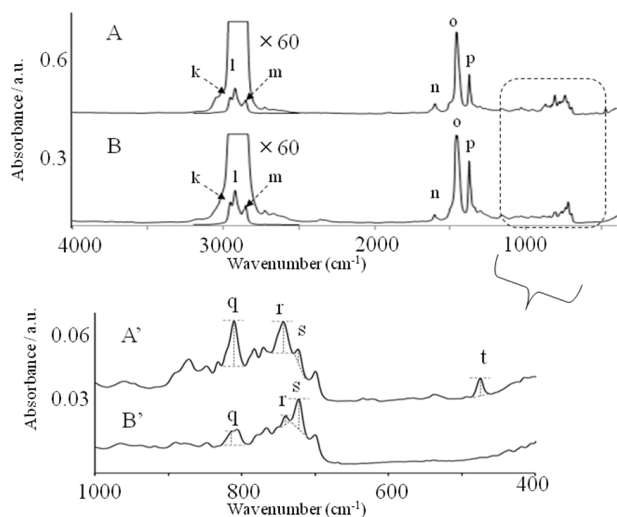


Figure 4
FT-IR of Heavy Oil (A) and Gas Oil (B) from 4000 cm⁻¹ to 400 cm⁻¹. FT-IR of Heavy Oil (A') and Gas Oil (B') from 1000 cm⁻¹ to 400 cm⁻¹.

The FT-IR spectra values for the heavy and gas oils ranging from 1,000 to 400 cm⁻¹ are shown in Figure 4. The absorption at 811 cm⁻¹ was assigned to the deformation vibration (2 adjacent hydrogen) (q), at 742 cm⁻¹ to the deformation vibration (4 adjacent hydrogen) (r), at 723 cm⁻¹ to the deformation vibration (s), and 475 cm⁻¹ to the out-of-plane ring vibration (t). The FT-IR results show the difference in the adsorption intensity between the gas and heavy oils for the absorptions at 811, 742, 723 and 475 cm⁻¹. The absorption of the gas oil increased in the order of 742 < 811 < 723 cm⁻¹, while the order of the heavy oil was 723 < 742 < 811 cm⁻¹. Furthermore, the absorption at 475 cm⁻¹ was recognized in the heavy oil, but not in the gas oil.

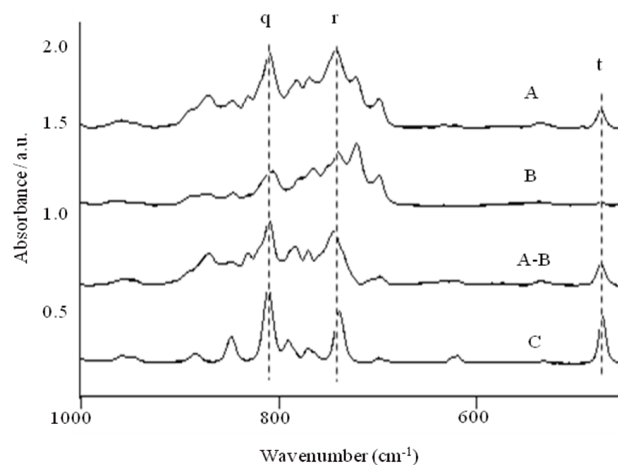


Figure 5
From 1000 cm⁻¹ to 400 cm⁻¹ FT-IR of Heavy Oil (A), Gas Oil (B), Difference Spectrum Between Heavy Oil and Gas Oil (A-B), and of Light Cycle Oil (C).

In order to examine the cause of the absorption at 811 cm⁻¹, the subtraction of the FT-IR spectra of the gas oil and heavy oil is shown in Figure 5(A-B). The FT-IR for 2-MN exhibited a high matching C ratio. The FT-IR result suggested that the difference between the gas and heavy oils may come from 2-MN. Figure 2i shows the structural formula for 2-MN. The main absorptions of 2-MN were observed at 849, 811, 742 and 475 cm⁻¹. Daniel et al^[11] reported the identification of 2-MN based on the characteristic absorption from 811 to 803 cm⁻¹. Moreover, Colthup et al^[12] suggested that 2-MN had characteristic absorptions ranging from 862 to 835 cm⁻¹, 835 to 805 cm⁻¹ and 760 to 735 cm⁻¹. Consequently, the difference between the gas and heavy oils derived from 2-MN is based on the absorptions at 811, 742 and 475 cm⁻¹. Moreover, the FT-IR for LCO showed the same absorption at 811 cm⁻¹ (deformation vibration (2 adjacent hydrogen)) (q), 742 cm⁻¹ (deformation vibration (4 adjacent hydrogen)) (r) and 475 cm⁻¹ (out-of-plane ring vibration) (t). These FT-IR data confirmed the GC-FID results. The difference between the gas and heavy oils was found in 2-MN and 1-MN when the heavy oil came from LCO. Consequently, the heavy oils discharged from ships and drifted on the seashore were discriminated from the original heavy oils and the gas oils.

CONCLUSION

The heavy oil floating on the sea with evaporated low-boiling-point compounds were discriminatively analyzed using biomarkers, such as hopanes, norhopanes and triaromatic sterane. The FT-IR and GC-FID analyses also discriminated the heavy oil from the gas oil. The gas and heavy oils exhibited a difference in terms of the naphthalene absorption ratio by the FT-IR analysis. Specifically, the absorption at 1603 cm⁻¹ for the heavy oil was higher than that for the gas oil. In the GC-FID

analysis, the heavy oil was clearly discriminated from the gas oil by the ratio of ((2-methylnaphthalene)+(1-methylnaphthalene))/tridecane. The heavy oil exhibited that of 1.0 or more, whereas the gas oil exhibited a value of less than 1.0. Methylnaphthalene in the heavy and gas oils partially arose from the LCO-derived substance. The results using GC-FID agreed with the FT-IR analysis results. Consequently, the heavy oils discharged from ships and drifted on the seashore were discriminated from the original heavy oils and gas oils.

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