

Geochemical differentiation using gas chromatography–mass spectrometry of the crude oil spilled from the Herbaysprit into the Tae Ann, Korea

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Abstract

Crude oil spilled from the Herbaysprit in December 2007 and contaminated Tae Ann Sound shoreline. A weathered oiled sediment collected at the spill area (Tai–Ann beach) from 3 months to 12 months after the spill. The fingerprinting and data interpretation techniques oil spill characterization and identification studies and environmental investigations discussed include oil spill identification protocol. Effects of weathering on hydrocarbon fingerprinting, recognition of distribution patterns of petroleum hydrocarbons, oil type screening and differentiation, analysis of specific marker compounds, determination of diagnostic ratios of specific oil constituents, are presented.

Introduction

Crude oil and petroleum products enter the environment are exposed to various environmental factors such as evaporation, dissolution, dispersion, photo–oxidation and biodegradation that change their chemical compositions. The collective term of processes that change oil composition is weathering, which can be divided into physical weathering (evaporation, dissolution, adsorption to particles, emulsification), biological weathering (mainly microbial degradation) and chemical weathering (photo degradation). The physical weathering processes such as evaporation and dissolution, which proceeds immediately after oils are spilled in the environment, are likely to transport compounds within and between environmental compartments (e.g., water, sediment, soil, air), whereas biological and chemical weathering processes degrade and chemically alter individual compounds within a compartment. Individual weathering processes remove compounds from the original oil in accordance to their physicochemical properties, thereby changing the properties of the residual oil (e.g., viscosity, biodegradability, toxicity), which subsequently affects the weathering rate. The long–term weathering processes at the environment are dominated by photo–oxidation and biodegradation.^{1–2)} Bulk properties such as total petroleum hydrocarbon (TPH) concentration, measured by

gas chromatography-flame ionization detection (GC-FID) and gravimetric analysis of the aliphatic, aromatic and polar fractions of weathered oil samples have been used frequently to estimate oil weathering. The most widely used strategies for the identification of oil pollutant in environmental samples require steps involving extraction, purification and analysis, as well as exhaustive analysis of the signals obtained.¹⁸ The analysis of total petroleum hydrocarbons (TPH) involves certain difficulties owing to the large number of possible interferences and the pitfalls involved in finding suitable reference standards.¹⁹⁻²⁰ In recent work, a methodology for the rapid detection of soil pollution by hydrocarbons using headspace-fast GC-MS.³⁾

In this work, The fingerprinting and data interpretation techniques oil spill characterization and identification studies and environmental forensic investigations discussed include oil spill identification protocol. A tiered analytical approach, generic features and chemical composition of oils, effects of weathering on hydrocarbon fingerprinting, recognition of distribution patterns of petroleum hydrocarbons, oil type screening and differentiation, analysis of specific marker compounds, determination of diagnostic ratios of specific oil constituents, are presented.

Experiment

Crude oil contaminated samples were dissolved in 40 ml of CH_2Cl_2 , mechanically shaken 15 min., and then ultrasonicated in pulse mode 10 min. The hydrocarbon determination was carried out in 5890 Series II coupled to a HP 5971A MS system. Operating conditions were as follows: Injection was done in the splitless mode for 1.0 min; an DB-5MS (5% phenyl-methylpolysiloxane capillary column (30m \times 0.25mm i.d., 0.25m film thickness, J&W) was used with an oven temperature of initial 45°C ramp to 300°C 8°C per min., then hold 10 min.

Results and discussion

The types and concentrations of specific oil constituents in environmental samples are dictated by the origin and nature of the spilled oil. For crude oil, the distribution depends greatly on its geological source; for weathered oil, the distribution depends not only on the weathering conditions, but also on the time of weathering (short-term or long-term). This approach was to identify diagnostic analyte ratios by calculating relative percent depletion for each analyte and The source and weathering ratio approach was then tested.

A. Total ion chromatogram **B. Saturated hydrocarbons(M/Z 85)**

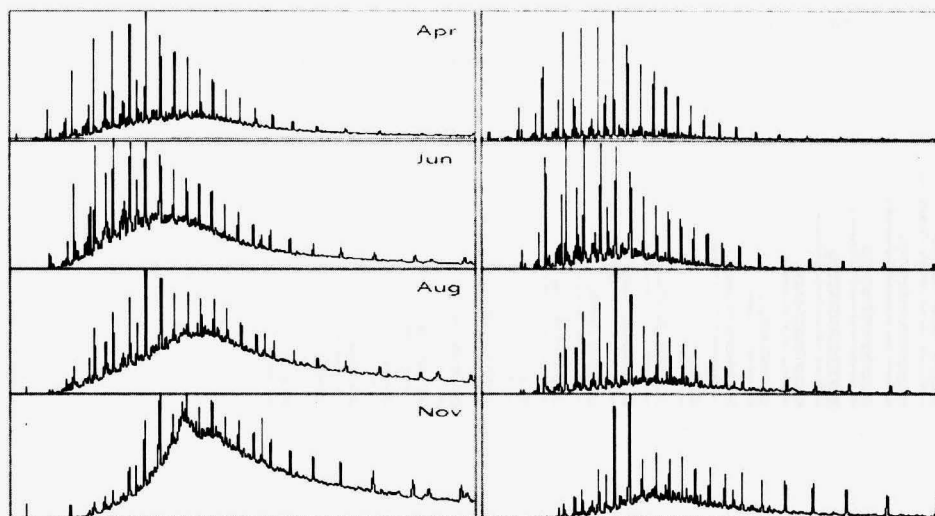


Fig. 1. Total ion chromatogram and extracted ion chromatogram for a degraded Tae Ann Slope crude oil extracted from a shoreline sediment sample collected from Apr. 2008 to Nov. 2008, from 3 months to 12 months after the Herbaysprit oil spill.

Fig. 1. shows that very neat profiles of nalkanes including isoprenoids with minimal interference from other petroleum hydrocarbons, C10–C34 linear alkanes with that number of carbon dependance of different saturated hydrocarbon. Also, they give clear information on the large differences in the saturated–compound distribution between samples. n -C8 to n -C17 region, and the abundance of n -alkanes gradually decreases as the carbon number increases. As weathering increases, the abundance of aliphatic components shifts to higher carbon numbers.

Fig. 2. shows the percent depletion of individual alkanes in a moderately degraded sample from that suite, collected in 3 ~ 12 months after the spill. As expected, shorter alkanes (n -C₁₀– n -C₂₈) are more depleted than the longer chain alkanes (n -C₂₈+), and the isoalkanes pristane and phytane are less depleted than the adjacent n -alkanes (n -C₁₇ and n -C₁₈). The differential depletion of n -alkanes to branched alkanes has been used as an indicator of biodegradation (ratios of n -C₁₇/pristane and n -C₁₈/phytane), but as can be seen from Fig. 2, the branched alkanes are themselves depleted, so such ratios substantially underestimate overall biodegradation in moderately degraded samples. Pristane and phytane are about equally depleted, so they are possible candidates for source ratios in weathered oil, but again their ready degradation makes them unsuitable in moderately to heavily degraded samples.

% depletion of n-alkanes,

(= $[1 - (C_i/C_0)(H_0/H_i)] \times 100$: H_0 , concentration of hopane source oil
 H_i , concentration of hopane in the degraded oil
 C_0 , analyte concentration of source oil
 C_i , analyte concentration of degraded oil)

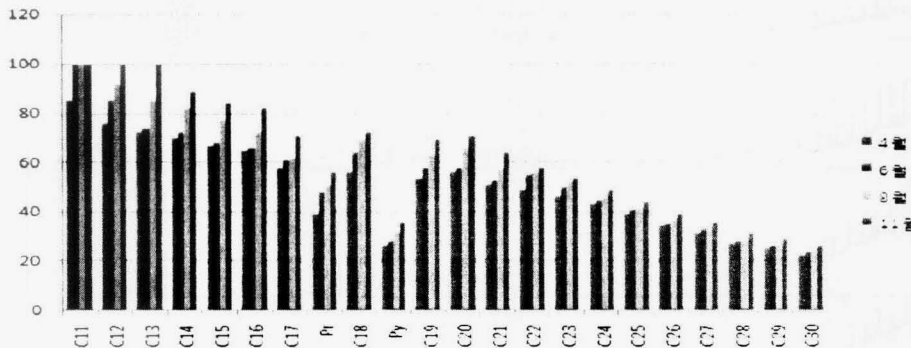


Fig. 2. Percent alkane depletion, based on the conservation of hopane, for a degraded crude oil extracted from a Tae Ann shoreline sediment samples. C_{11} - C_{30} are linear alkanes with that number of carbons; pr and ph are pristane and phytane.

Conclusion

Capillary gas chromatographic-mass spectrometric technique for the determination of types and classes including C_{11} through C_{40} normal alkanes, the isoprenoids pristane and phytane in crude oil. The analytical data and results obtained by using these methods are important and essential in differentiating individual crude oils, monitoring the changes in oil composition during weathering, understanding the fate and behaviour of the spilled oil in the environment, and assessing the damage of spilled oil to the natural resources.

Acknowledgment

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Referances

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