Evaluation of Total Petroleum Hydrocarbon in Soil Using LC with Fraction Collector and GC/MS

Application

Environmental

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Abstract

Normal-phase liquid chromatography (NPLC) and capillary gas chromatography with mass spectrometry are employed to evaluate the total petroleum hydrocarbon (TPH) in the soil contaminated by crude oil. In this paper, paraffins and mono-aromatic and multi-aromatic compounds present in the sample were first separated by NPLC into different classes of compounds according to their individual polarities, and fractions were collected for subsequent analysis by GC/MS, separated by boiling point, and identified by their unique mass spectra.

Introduction

Pollution due to oil spills happens frequently all over the world. Positive identification of the source is a critical part of establishing liability for cleanup costs and environmental damages. Because the spill is subject to time-based alteration by weathering (dissolution or evaporation), chemical degradation (effects of sunlight, heat, air, and soil chemistry), and biological alteration (impact of microorganisms) it has become more and more important to map these effects. Scientists have developed diverse technologies to perform the comprehensive evaluation analysis of TPH in environmental matrices. DIN 38 409 H18 [1] is the official method using infrared spectrometry. Robert [2] introduced a comprehensive two-dimensional gas chromatography to track the weathering of an oil spill. A portable GC/MS method was presented to determine the concentration of TPH from unresolved signals in short test runs in the field.

Sjaak [3] introduced group-type characterization of mineral oil samples by two-dimensional comprehensively coupled LC x GC-ToF MS. The interface between LC and GC/MS consisted of a 100-µL syringe, with two side entrances/exits in the upper part of the barrel, installed in an injection robot. A stop-flow mode of LC was adopted during the GC/MS analysis.

In this paper, we employed a fraction collector to replace the complex interface between HPLC and GC/MS and applied a combination of NPLC and GC/MS to evaluate the TPH in the soil contaminated by crude oil.

Experimental

Instrumentation and Conditions

Agilent 1200 Series LC, consisting of:

G1379B	Micro vacuum degasser
G1312B	Binary pump SL
G1367C	High-performance autosampler SL
G1316B	Thermostatted column compartment SL with 6- or 10-port 2-position switching valve
G1315C	UV/VIS diode array detector SL
G1364C	Fraction collector (analytical scale)

ChemStation 32-bit version B.02.01-SR1

Agilent 6890GC with 5975B MSD, consisting of:

G1540N	6890N network GC system with options: 201 MSD interface
G3243A	5975B inert MSD/DS perf turbo EI bundle
G3397A	Ion gauge/controller for use with 5975 MSD
G2913A	7683B autoinjector module
G2614A	7683 autosampler tray module

MSD Chemstation version D.03.00 with NIST 05 MS Library version 2.0d

The LC and GC/MS operating conditions are listed in Table 1.

Sample Preparation

The crude oil sample was from the Daqing, China, oil field and contributed by Sinopec Shanghai Gaoqiao Petrochemical Corporation.

The sample was prepared by mixing a 1 g oil sample with a blank soil sample and depositing the mixture in a fume hood for 2 days. Next, 50 mL of hexanes was added and the sample was extracted in an ultrasonic water bath for 1 hour. The extract was filtered, and 10 mL of filtrate was pipetted and then evaporated under a nitrogen stream to less than 1 mL. The extract was then made up with hexanes to 1 mL, and the solution was injected into NPLC for analysis.

Operation of Column Switching Valve and Fraction Collector of NPLC

The crude oil sample was so complex that a column switching valve was employed to backflush the analysis column in the NPLC system. To approximately evaluate the retention time of every group of compounds, a system calibration standard was used, which was composed of cyclohexane, o-xylene, dibenzothiophene and 9-methylanthracene, as generally outlined in ASTM Methods D6379 and D6591. The separation of the system calibration standard is shown in Figure 1. To minimize the total analysis time, the LC eluate of the first 3 min was sent to waste. Afterwards, fractions were collected every 0.5 min by the fraction collector. After collecting the fractions that contained the compounds of interest, the column was switched to backflushing mode for cleaning and the LC run was closed after the baseline stabilized.

Results and Discussion

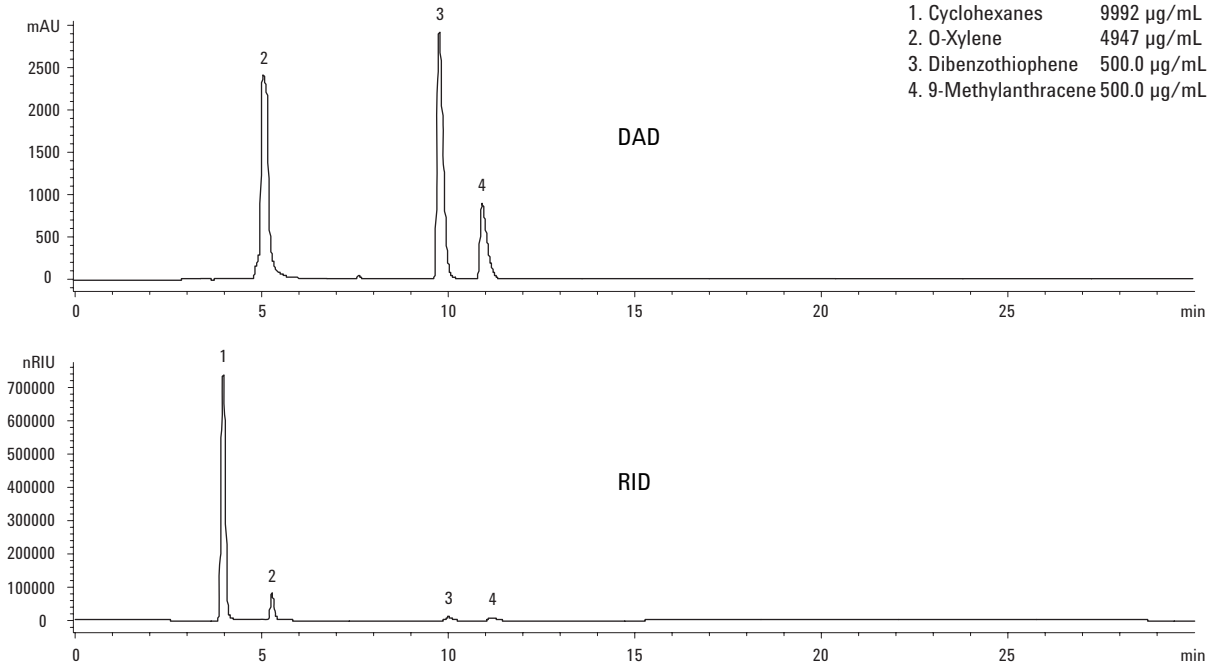
The soil sample extract was separated into different groups by normal phase liquid chromatography according to their polarities, as displayed in Figure 2. A total of 23 fractions were collected, which were injected into the GC/MS system for subsequent separation according to their boiling point and identification according to their characteristic mass fragments. A total ion chromatogram (TIC) of typical paraffins and mono-aromatic, bi-aromatic, and tri-aromatic compounds is depicted, respectively, in Figure 3. Through the identification by mass spectra, the first group with a retention time range of 3.7 to 4.7 min in LC chromatography contained paraffins; the second group, with a retention time range of 4.7 to 6.2 min, contained mono-aromatic compounds; the third group, with a retention time range of 6.2 to 11.2 min, contained bi-aromatic compounds; and the fourth group, with a retention time range of 11.2 to 13.7 min, contained tri-aromatic compounds. No aromatic compounds eluted at the retention time range from 13.7 min to the end.

Table 1. LC and GC/MS Operating Conditions

LC	**Agilent Technologies 1200SL**		
Mobile phase	Hexanes		
Flow rate	0.8 mL/min		
Wavelength	210 nm		
Injection volume	100 µL		
Mode	Isocratic		
Column	Agilent ZORBAX NH_2		
	4.6 mm x 250 mm, 5 µm		
Analysis time	30 min		
Column temperature	35 °C		
Column switching valve	Backflushing off		
Column switching timetable	Time	Column	
	15.00 min	Backflushing on	
	30.00 min	Backflushing off	
Fraction trigger mode	Use timetable		
Fraction collector timetable	Time	Trigger mode	Time slices
	3.70 min	Time-based	0.5 min
	15.00 min	Off	–

GC	**Agilent Technologies 6890N**
	7683 autoinjector and tray
Autoinjector	
Sample washes	3
Sample pumps	6
Injection volume	1 µL
Syringe size	5 µL
Preinjection solvent A	0
Preinjection solvent B	3
Post-injection solvent A	0
Post-injection solvent B	3
Viscosity delay	0 s
Plunger speed	Fast
Preinjection dwell	0 min
Post-injection dwell	0 min
Sampling depth	Disable

Inlet	**EPC**
Injection type	Splitless
Inlet temperature	250 °C
Pressure	7.61 psi
Purge flow	50.0 mL/min
Purge time	0.75 min
Total flow	54.0 mL/min
Gas saver	On
Saver flow	20.0 mL/min
Saver time	2.00 min
Gas type	Helium
Oven	
Initial temperature	50 °C
Initial time	1.00 min
Ramp rate	30.00 °C/min
Final temperature	300 °C
Final hold	2.00 min
Total run time	11.33 min
Equilibration time	0.5 min
Column	
Type	HP 5-ms
Length	30 m
Diameter	0.25 mm
Film thickness	0.25 µm
Mode	Constant flow
Initial flow	1.0 mL/min
MSD	**Agilent Technologies 5975B inert**
Solvent delay	4 min
Tune file	Atune.U
Mode	Scan
Solvent delay	3.00 min
EM voltage	Atune voltage
Low mass	45.0 amu
High mass	450.0 amu
Threshold	150
Sampling	2
Scans	3.54
Quad temperature	150 °C
Source temperature	230 °C
Transfer line temperature	280 °C



Mobile phase	Hexanes
Flow rate	0.8 mL/min
Detection	DAD and RID
UV wavelength	210 nm
Analysis time	30 min (backflush @ 15 min)
Column	Agilent ZORBAX NH_2 4.6 x 250 mm, 5 µm
Method	Follow ASTM D6379 (or D6591)
Sample	System Calibration Standard
Sample size	10 µL
Column temperature	35 °C

Figure 1. Chromatogram of standard solution.

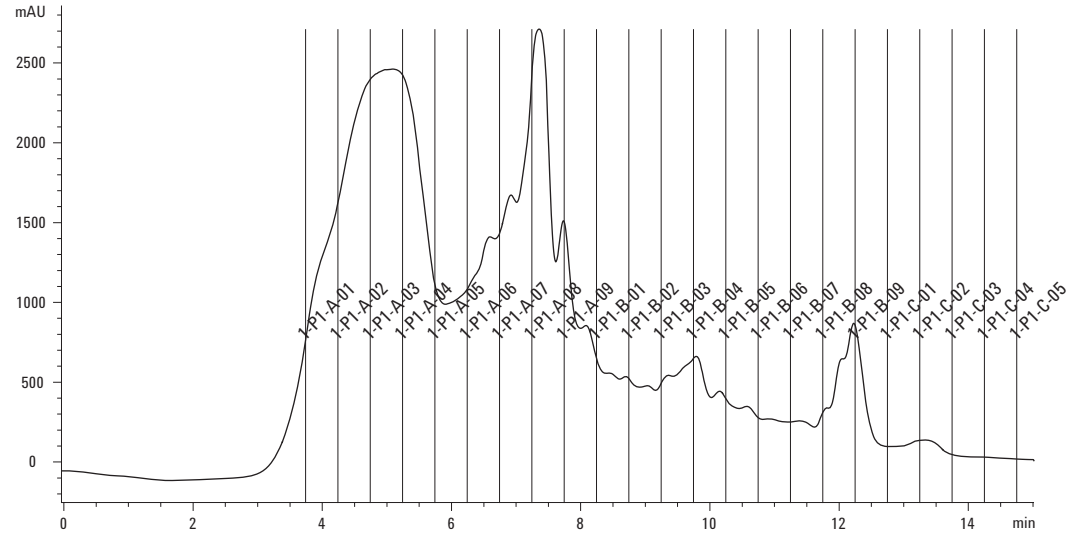


Figure 2. Chromatogram of soil sample extract and factions collected in different vials.

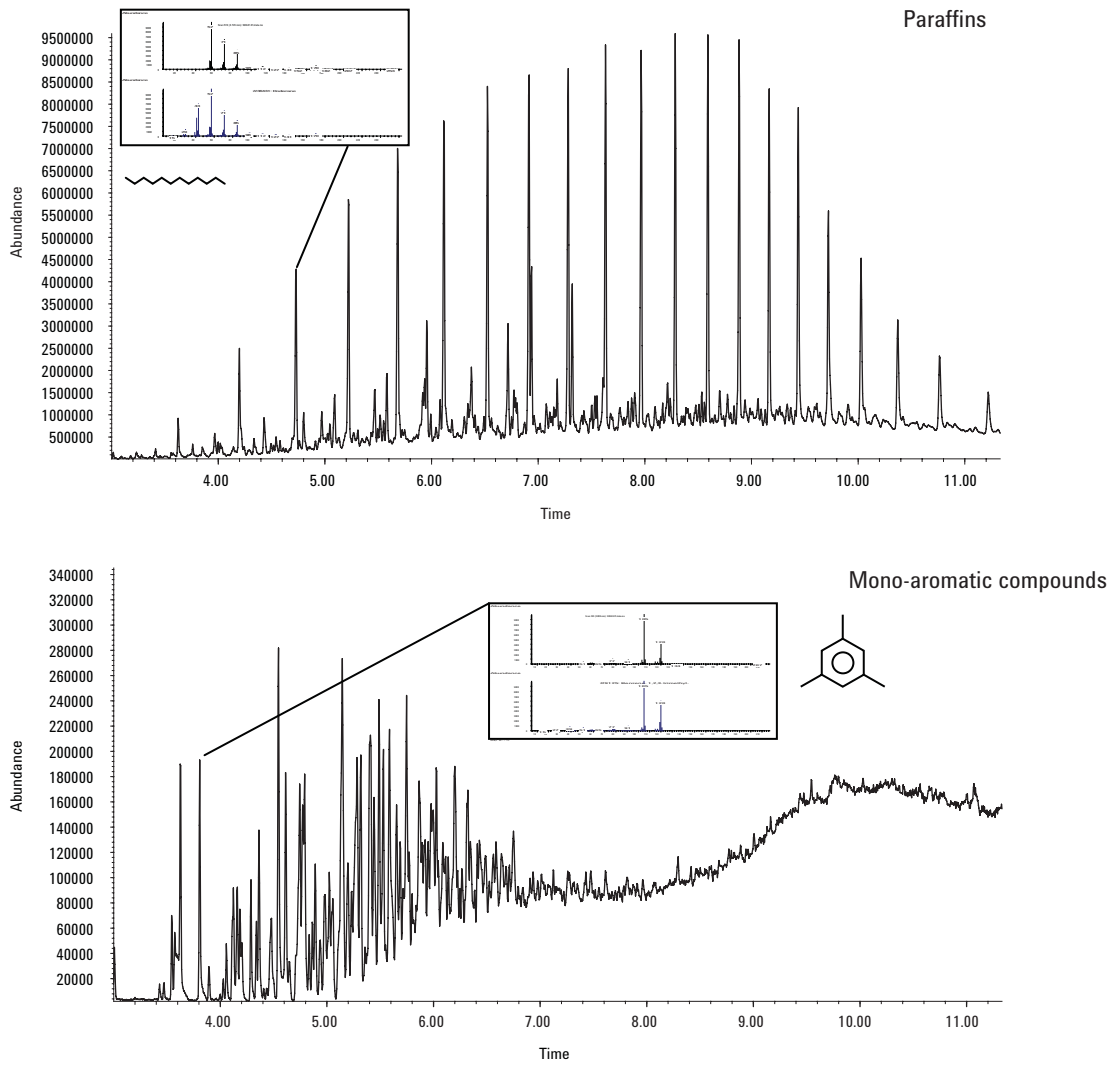


Figure 3. Total ion chromatogram of typical fractions including paraffins and mono-, bi-, and tri-aromatic compounds.

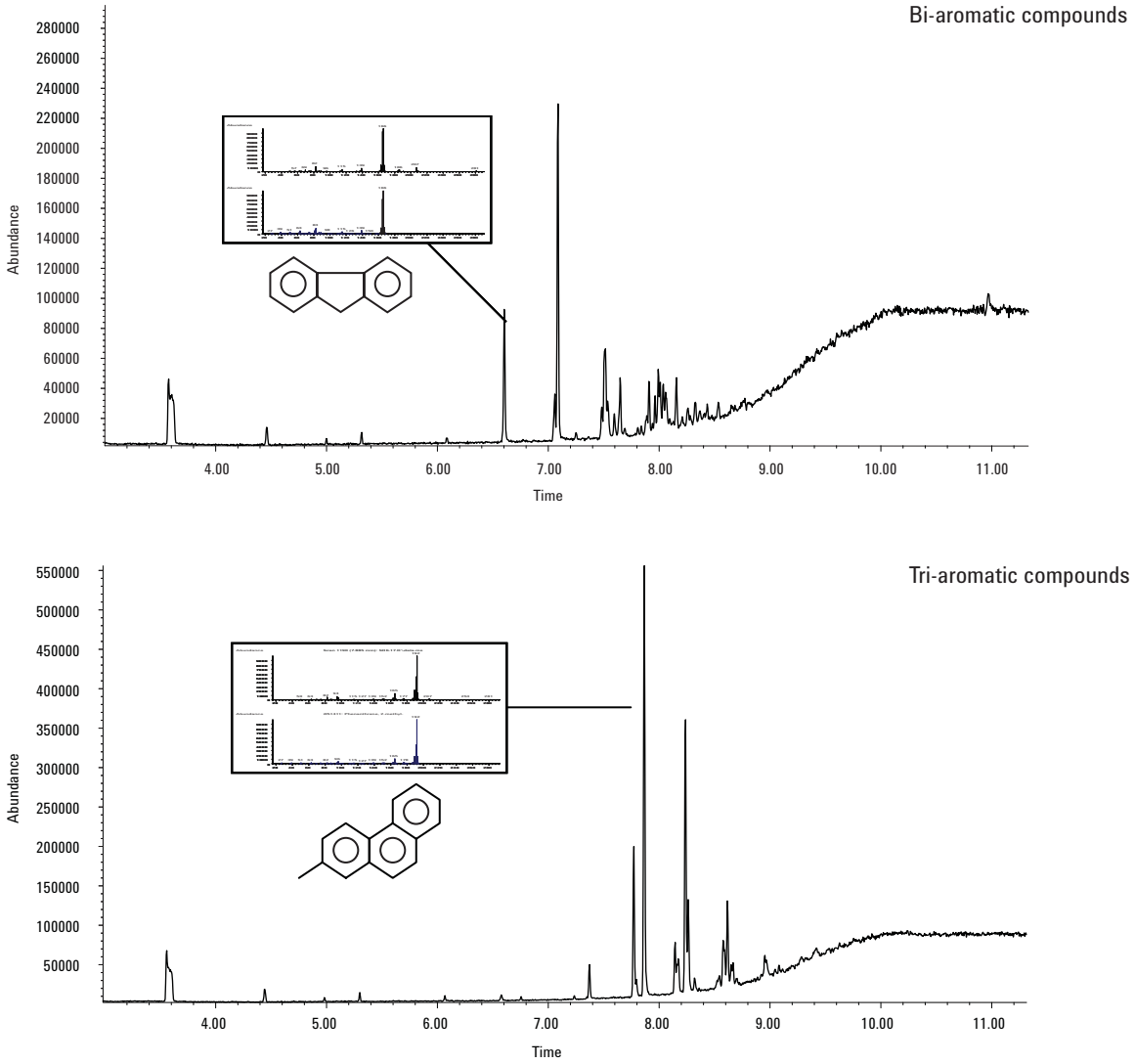


Figure 3. Total ion chromatogram of typical fractions including paraffins and mono-, bi-, and tri-aromatic compounds. (continued)

	Vial Position	Time Slices
Paraffin	1-P1-A-01	3.7 to 4.2 min
Mono-aromatic compounds	1-P1-A-04	5.2 to 5.7 min
Bi-aromatic compounds	1-P1-B-04	9.7 to 10.2 min
Tri-aromatic compounds	1-P1-B-08	11.7 to 12.2 min

Conclusions

The separations by NPLC and GC are based on polarity and boiling point, respectively. Mass spectra could provide the information on the molecular structure; therefore, the combination of NPLC and GC/MS could be used to evaluate the complex matrix. In this work, an LC with a fraction collector performed the separation of classes of paraffins and mono-, bi-, and tri-aromatic compounds and collected time-based fractions into individual sample vials. The fractions were injected into the GC/MS for identification. A soil sample contaminated by crude oil was analyzed by this method and the results showed the detailed component information of every typical class, based on fractionation by polarity, to evaluate the total petroleum hydrocarbon in soil.

References

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