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Differentiation of the source of spilled oil and monitoring of the oil weathering process using gas chromatography–mass spectrometry

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Abstract

Methods described use high-performance capillary gas chromatography–mass spectrometry (GC–MS) operating mainly in the selected-ion monitoring (SIM) mode for oil analysis. The methods have been applied to the characterization of crude oils, weathered oils, biodegradation oils, and oil-spill-related environmental samples with different compositions, nature, and concentrations. Using GC–MS enables the identification and quantitation of specific target petroleum hydrocarbons including C_8 through C_{40} normal alkanes, the isoprenoids, BTEX and alkyl benzene, target polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues, and biomarker triterpanes and steranes. The analysis of these target compounds and/or compound groups is important and essential for oil-spill monitoring. The analytical data have been successfully used for the differentiation of oils, tracking the source of long-term spilled oils, monitoring the oil weathering and biodegradation process under variable environmental conditions, and the determination of the weathering percentages of very heavily weathered oil samples by the selective use of biomarker parameters. Compared to some other traditional methods which were originally designed for industrial waste and hazardous waste, the methods described here are more selective and give a better representation of the true oil composition, and hence are more defensible.

1. Introduction

Oil contamination of soil and water caused by transportation accidents and leakages is a consequence of the growing industrialization and demands for energy. Incidents of this type have created a global public awareness of the risks and danger associated with oil spills and driven the search for effective and environmentally safe cleanup treatments. During the last decade, a large progress has been made in oil-spill cleanup techniques including physical, chemical and biological methods [1]. Among these techniques, bacterial degradation of petroleum hydrocarbons has been widely recognized. For example, biodegradation was used for the 1989 EXXON VALDEZ spill cleanup [2,3]. Appropriate selection and application of standardized and comparable analytical methods are required to assess the damage to the environment and natural resources caused by the released petroleum, to

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provide an effective cleanup strategy, to evaluate the efficacy of bioremediation products and other oil-spill treating products, and to understand the behaviour and fate of spilled oil in the environment and to predict the potential long-term impact of the spilled oil.

Crude oil and oil-spill-related samples are extremely complex mixtures in which the components range from simple alkanes to complex asphaltic components, the boiling points of which vary over a wide range from a few to several hundred degrees. As soon as oil is spilled into the environment the processes of volatilization, dissolution, microbial and photochemical degradation act to change its composition. Consequently, the chemical analysis methods employed should yield sufficient accuracy and compositional detail (especially with respect to the key toxic compounds, because the effects of spilled oil on the environment are strongly related not only to the gross amount of oil, but also to the levels of those key toxic compounds) to answer the specific questions to be answered in an environmental assessment study.

In recent years, major advances have been achieved in the analytical methods and techniques used for oil analysis. Various adsorbents (including silica gel, alumina, florisil, combination of silica and alumina, and solid-phase extraction) and various eluting solvents have been used to fractionate oil into saturated, aromatic, and polar groups [4,5]. The fractions are then analyzed using techniques, e.g. gravimetric methods, gas chromatography (GC), infrared spectroscopy (IR), ultraviolet (UV) and fluorescence spectroscopy, and mass spectrometry (MS). Among these techniques, capillary GC is most widely used. Over the last decade GC with flame ionization detection (FID) has been employed in oil-spill studies for the determination of *n*-alkanes, isoprenoids, and the total petroleum hydrocarbons. However, because of its nonspecificity FID may produce erroneous results, due to e.g. analyte coelution and matrix interference, when it is used for the determination of polycyclic aromatic hydrocarbon compounds (PAHs). Thus, the compound-specific data and information obtained from GC–FID is limited: quantitation of aromatic compounds can be only partially achieved, and identification and quantitation of biomarker compounds would be almost impossible. As for the gravimetric, IR, and UV methods, they only provide estimates of the whole fractions.

For weathering studies, monitoring the changes in the chemical composition of the spilled oil is of crucial importance, especially when there is a prolonged period of weathering. Also for oil source identification, detailed knowledge of the chemical composition is needed, since each type of oil has a different component distribution. Therefore, positive conclusions about oils sources and the fate of the oil in the environment can only be obtained through comparison of their chemical composition, especially through the so called "pattern-recognition" plots involving more than 100 important individual oil components and component groupings [6]. All of these demands point to GC–MS fingerprinting as the most appropriate technique.

High-performance capillary GC–MS, which combines chemical separation by GC with spectral resolution by MS, allows for specific target compound determination. This is especially important for the determination of the alkyl aromatic homologous compounds (C_1- through C_6-alkyl groups of benzene, naphthalene, and other PAHs) and biomarker compounds (triterpanes and steranes) in oil. For quantitation of target compounds, the selected-ion monitoring (SIM) mode of GC–MS is mostly selected. GC–MS operating in the SIM mode shows several distinct advantages. The method detection limits for the target analytes are generally lower by almost an order of magnitude than those produced by conventional full-scan GC–MS. The reduction in number of ions per scan in GC–SIM-MS analysis increases the sensitivity of the instrument, thereby lowering the instrument detection limit. Furthermore, the use of GC–SIM-MS often increases the linear range of the instrument for low-concentration analytes. Over the past several years, new low-cost GC–MS systems have made GC–MS analysis feasible and attractive for

many analytical laboratories, and this trend will continue.

In recent years, the Emergencies Science Division (ESD) of Environment Canada in cooperation with the US Minerals Management Service has conducted projects to investigate various countermeasures in responding to oil spills. The goal of one such project is to develop analytical methods to identify, characterize and quantify oil samples with respect to their composition, nature and concentrations. Using this method, Alberta Sweet Mix Blend (ASMB) oil has been extensively characterized [7]; long-term weathered oil samples have been identified and their fate and persistence in the environment have been studied through pattern recognition of biomarker compounds [8,9]; the effects of weathering on the chemical composition of oil have been quantitatively understood [6] and determination of weathering percentages of oil in highly-weathered oil sediment samples has been achieved using C_{29}-$\alpha\beta$- and C_{30}-$\alpha\beta$-hopane in the source oil as internal oil references [9]; screening procedures have been developed for assessing the efficacy and toxicity of oil-spill bioremediation agents by analyzing hundreds of biodegradated oil samples [10], and identification of alkyl benzenes in oil and direct determination of BTEX (the collective name for benzene, toluene, ethylbenzene, and the xylene isomers) and (BTEX + C_3-benzenes) using GC–MS has been achieved [11]. The high chemical and spectral separation power of GC–MS allows us to identify, characterize and quantify over 100 saturated hydrocarbons, over 50 alkyl benzene homologues and over 60 PAH compounds, and over 50 biomarker compounds in crude oils, weathered oils, biodegradation oils, and various oil-spill-related environmental samples. The focus of this analytical technique is to identify and quantify target compounds as accurately as possible with minimal interference so that more complete and precise information on the changes in chemical composition and the effects of various factors on oil degradation can be monitored and assessed as the oils undergo weathering and degradation processes.

2. Experimental

2.1. Capillary gas chromatography–mass spectrometry

Analyses were performed on a HP 5890 GC–5972 MSD. System control and data acquisition was achieved by HP G1034C MS ChemStation (DOS series). The MSD was operated in the scan and selected-ion monitoring (SIM) modes to obtain spectral data for the identification of the components, and in the SIM mode for quantitation of target compounds. The SIM mode involves monitoring those specific, preselected ions which are useful for identifying, characterizing, and quantifying the oil components of interest. Table 1 lists important oil fingerprinting compounds and compound classes. As shown, the target compounds include: *n*-alkanes (*n*-C_8 to *n*-C_{40}) plus five selected–and often the most abundant–isoprenoids (2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane, norpristane, pristane and phytane); PAHs and their alkylated homologues; biomarker compounds triterpanes and steranes. Sometimes the volatile aromatic hydrocarbons BTEX and C_2- through C_5-benzenes and polar compounds may be included as well, depending on the type of oil spilled and on the environmental assessment requirement. The columns used were 30 m × 0.25 mm I.D., 0.25 μm HP-5 fused-silica columns. The chromatographic conditions were as follows: carrier gas, helium (1.0 ml/min); injection mode, splitless; injector and detector temperature, 290°C and 300°C, respectively; temperature program for *n*-alkane distribution, alkylated PAHs and biomarker compounds, 50°C for 2 min, then 6°C/min to 300°C, hold 16 min; temperature program for BTEX and target alkyl benzenes, 35°C for 2 min, then ramp at 10°C/min to 300°C and hold 10 min.

2.2. Oil and oil samples

Alberta Sweet Mix Blend (ASMB) oil is the reference oil used for dispersant testing in ESD. This oil has been extensively characterized and

Table 1
Petroleum fingerprinting analytes of interest

Aliphatics hydrocarbons	Target ions	Target PAHs	Target ions	Biomarkers compounds	Target ions
n-C8	85, 71	Naphthalene	128	*Triterpanes*	
n-C9	85, 71	C1-naphthalene	142	Tricyclic terpanes	191
n-C10	85, 71	C2-naphthalene	156	Tetracyclic terpanes	191
n-C11	85, 71	C3-naphthalene	170	Pentacyclic terpanes	191
n-C12	85, 71	C4-naphthalene	184	$C_{27}H_{46}$(Ts)	191
n-C13	85, 71	Phenanthrene	178	$C_{27}H_{46}$(Tm)	191
n-C14	85, 71	C1-phenanthrene	192	$C_{28}H_{48}$	191
n-C15	85, 71	C2-phenanthrene	206	$C_{29}H_{50}$ $\alpha\beta$-	191
n-C16	85, 71	C3-phenanthrene	220	$C_{30}H_{52}$ $\alpha\beta$-	191
n-C17	85, 71	C4-phenanthrene	234	$C_{31}H_{54}$ 22*S*/22*R*	191
Pristane	85, 71	Dibenzothiophene	184	$C_{32}H_{56}$ 22*S*/22*R*	191
n-C18	85, 71	C1-dibenzothiophene	198	$C_{33}H_{58}$ 22*S*/22*R*	191
Phytane	85, 71	C2-dibenzothiophene	212	$C_{34}H_{60}$ 22*S*/22*R*	191
n-C19	85, 71	C3-dibenzothiophene	226	$C_{35}H_{62}$ 22*S*/22*R*	191
n-C20	85, 71	Fluorene	166		
n-C21	85, 71	C1-fluorene	180	*Steranes*	
n-C22	85, 71	C2-fluorene	194	C_{27}20 *R*/*S*-cholestanes	217, 218
n-C23	85, 71	C3-fluorene	208	C_{28}20 *R*/*S*-ergostanes	217, 218
n-C24	85, 71	Chrysene	228	C_{29}20 *R*/*S*-stigmastanes	217, 218
n-C25	85, 71	C1-chrysene	242		
n-C26	85, 71	C2-chrysene	256	*Surrogates and standards*	
n-C27	85, 71	C3-chrysene	270	1. Surrogates	
n-C28	85, 71	Biphenyl	154	d10-Acenaphthene	164
n-C29	85, 71	Acenaphthylene	152	d10-Phenanthrene	188
n-C30	85, 71	Acenaphthene	153	d12-Benz[*a*]anthracene	240
n-C31	85, 71	Anthracene	178	d12-Perylene	264
n-C32	85, 71	Fluoranthene	202		
n-C33	85, 71	Pyrene	202	2. Internal Standards	
n-C34	85, 71	Benz[*a*]anthracene	228	d14-Terphenyl	244
n-C35	85, 71	Benzo[*b*]fluoranthene	252	C_{30}-$\beta\beta$-Hopane	191
n-C36	85, 71	Benzo[*k*]fluoranthene	252		
n-C37	85, 71	Benzo[*e*]pyrene	252	3. QC Standards	
n-C38	85, 71	Benzo[*a*]pyrene	252	*n*-alkane standards	
n-C39	85, 71	Perylene	252	SRM 1491	
n-C40	85, 71	Indeno(1,23-cd)pyrene	276	alkyl-benzene std	
		Dibenz[*a.h*]anthracene	278	triterpane and sterane std	
BTEX and C3-benzenes	78,91,105	Benzo[*ghi*]perylene	276		

detailed identification and quantitation results have been reported elsewhere [4,7]. Other oils were obtained from various sources during the period 1985–1994 and stored in the cold room of this laboratory.

BIOS (Baffin Island Oil Spill, 12 year old) and 22-year-old Arrow oil sediment samples (except the sample BIOS No. 8 which was a water sample) were collected from Baffin Island and the north shore of Chedabucto Bay of Canada, respectively. The sediment and water sample preparation, extraction, cleanup, and fractionation have been described elsewhere [4,7–9].

2.3. Quantitation and analysis quality control

Initially, five-point calibration curves were established for analytes and internal standards, demonstrating the linear range of the analysis. The relative response factor (RRF) and relative

standard deviation (R.S.D.) for each hydrocarbon component was calculated relative to the internal standard. The GC–MS instrument was carefully maintained and tuned daily to achieve the required sensitivity. An instrument blank and standard solutions (which were composed of authentic *n*-alkanes plus isoprenoids, or authentic target PAH compounds, or authentic alkyl benzenes, or authentic hopanes and steranes, depending on the analysis requirement) were analyzed before and after each sample batch (approximately 10 samples) to monitor accuracy and precision. The RRFs obtained from the daily calibration standards should fall within 25% of the corresponding initial calibration curve values [8,12]. If not, a five-point calibration curve would be repeated for that compound prior to sample analysis.

The calibration standard for *n*-alkane analysis was composed of C_8- through C_{40}-*n*-alkanes, pristane, and phytane. 5-α-Androstane was used as the internal standard.

Quantitation of BTEX and C_3-benzenes, target PAHs, alkylated PAH homologues was performed in the SIM mode with RRFs for each compound determined during instrument calibration. PAH alkyl homologues were quantified by using the straight baseline integration of each level of alkylation. Although the alkylated homologue groups can be quantitated using the RRF of the respective unsubstituted parent PAH compounds, it is preferable to obtain the RRFs directly from alkylated PAH standards, when commercially available. In this work, the RRFs obtained for 1-methyl-naphthalene, 2-methyl-naphthalene, 2,6-dimethyl-naphthalene, 2,3,5-trimethyl-naphthalene, and 1-methyl-phenanthrene were used for quantitation of 1-methyl-naphthalene, 2-methyl-naphthalene, C_2-naphthalene, C_3-naphthalene, and C_1-phenanthrene in oil, respectively. The RRFs of 2,3,5-trimethyl-naphthalene and 1-methyl-phenanthrene were used for quantitation of C_4-naphthalene, and C_2-, C_3-, and C_4-phenanthrenes, respectively. The selection criteria for the integration and reporting of each alkylated homologue were based primarily on pattern recognition and the presence of selected confirmation ions.

The average RRF for the biomarker compound C_{30}-17β(H)21α(H)-hopane was determined relative to the internal standard C_{30}-17β(H)21β(H)-hopane. The average RRF for C_{30}-17β(H)21α(H)-hopane (*m/z* 191) was used for quantitation of C_{30}-17α(H)21β(H)-hopane and other triterpanes (in the range C_{19}–C_{35}) in the oil sample. For quantitation of steranes, due to the lack of availability of appropriate deuterated steranes, C_{29}-20*R*-$\alpha\alpha\alpha$-ethylcholestane was used and monitored at *m/z* 217 to obtain the RRF relative to C_{30}-17β(H)-21β(H)-hopane monitored at *m/z* 191, and then the average RRF of C_{29}-20*R*-$\alpha\alpha\alpha$-ethylcholestane was used for estimation of sterane compounds in the oil.

3. Results and discussion

3.1. Saturated hydrocarbons

The types and concentrations of specific oil constituents in environmental samples are dictated by the origin and nature of the spilled oil. Each oil has a different "fingerprint" and compound distribution. 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). The low-molecular-mass (M_r) saturated hydrocarbons in weathered oil samples may be lost and some degradation-resistant compounds may at the same time increase in relative concentration because of the weathering effects. This results in significant changes in the chemical composition and concentration of the oil.

Saturated hydrocarbons are major constituents of petroleum. Although the *n*-alkanes and isoprenoids are generally not of toxicological concern, identification and quantitation of these target analytes would be valuable to serve the following purposes [6,9,13,14]: tracer of the presence of spilled oil; basic spilled-oil fingerprints; indicator of the fate of the spilled oil and the changes in chemical composition due to weathering; and monitoring the loss of spilled-oil components by evaporation and/or biodegrada-

tion in environmental samples. In addition, these chemical data can also be used to differentiate the specific spilled oil from pre-spill or background pollution sources in environmental samples. Some biodegradation indicators relative to the spilled source oil (such as the n-C_{17}/pristane, and n-C_{18}/phytane ratios) can provide information on the effect of microbial biodegradation on the loss of hydrocarbons in an impacted area. Fig. 1 shows n-alkane distribution chromatograms of three different oils obtained by GC–MS (m/z 85) measurement: ASMB oil (B), California oil (D), and Orimulsion (F). For comparison purposes, the GC–FID chromatograms (A, C, and E) are also presented in Fig. 1. The GC–MS chromatograms of saturated hydrocarbons (m/z 85, 71, and 57) show very neat profiles of n-alkanes including isoprenoids with minimal interference from other petroleum hydrocarbons. Also, they give clear information on the large differences in the saturated-compound distribution between oils, which is indicated by the distribution of the n-alkanes and by the profile of the hump. It can be readily seen from Fig. 1 that these three oils are very different, not only because of their different distribution patterns and profiles, but also because of the significantly higher concentration of branched saturates relative to normal alkanes in California oil. As for Orimulsion, no noticeable n-alkanes are seen from its GC–FID and GC–MS chromatograms.

Fig. 2A–F shows the n-alkane distribution of the ASMB oils (determined by GC–FID) which were artificially weathered to varying percentages of weight loss (w/w) using a lab-scale rotary evaporation technique [6]. For the source ASMB oil, the most abundant n-alkanes are found in the n-C_8 to n-C_{17} region (Fig. 2A), 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. For example, the n-alkane with the highest concentration is n-C_9 in 0% weathered oil (4.8 mg/g oil) and n-C_{17} in 44.5% weathered oil (6.7 mg/g oil), respectively. It is noted that even though the ASMB oil was weathered from 0% to 45%, the sum of the n-alkanes for the six weathered ASMB oil samples did not change significantly (range, 70–76 mg/g oil). This can be explained by the combination of two opposite effects: one being the loss of low-M_r aliphatic components by evaporation, the another the buildup of high-M_r aliphatic components by oil volume reduction. The ratios of n-C_{17}/pristane, n-C_{18}/phytane, and pristane/phytane are virtually unaltered because these compounds have about the same volatility. It has been demonstrated, however, that the ratios of n-C_{17}/pristane and n-C_{18}/phytane significantly decreased when biodegradation was involved [8,9,15,16]. This is because biodegradation preferentially removes n-C_{17}, n-C_{18} and other normal alkanes from oil samples. Therefore, for less weathered or short-term weathered oil, the traditional diagnostic ratios such as n-C_{17}/pristane, n-C_{18}/phytane, and pristane/phytane are useful to identify the source of the oil and to assess the effect of microbial degradation and weathering of the oil, but they would be of less value for highly weathered and degraded oil samples (usually under long-term environmental exposures) due to the nearly complete loss of not only n-alkanes, but also of isoprenoids and most PAH compounds. Fig. 3 illustrates this case well. Fig. 3 (top) shows the GC–MS chromatogram of the m/z 85 fragment of weathered Arrow oil, which shows a mixture dominated by a homologous series of n-alkanes ranging from n-C_9 to n-C_{40} with a maximum around n-C_{20} to n-C_{22}. Isoprenoids are also present, with pristane and phytane being the most abundant. In sharp contrast, the n-alkanes, including the five isoprenoids, were nearly completely lost in a 22-year-old Arrow oil sample. The unresolved complex mixture (UCM) dominates the total peak area (Fig. 3, bottom). This dominated UCM indicates the sample has been very heavily weathered (indicator of weathering degree) and its chemical composition has undergone extreme alteration. Definitely, this kind of chromatogram cannot provide much information on the source of the spilled oil.

3.2. BTEX and alkyl benzenes

The composition and concentration of BTEX and alkyl benzene compounds (being important constituents of oil and probably the most volatile

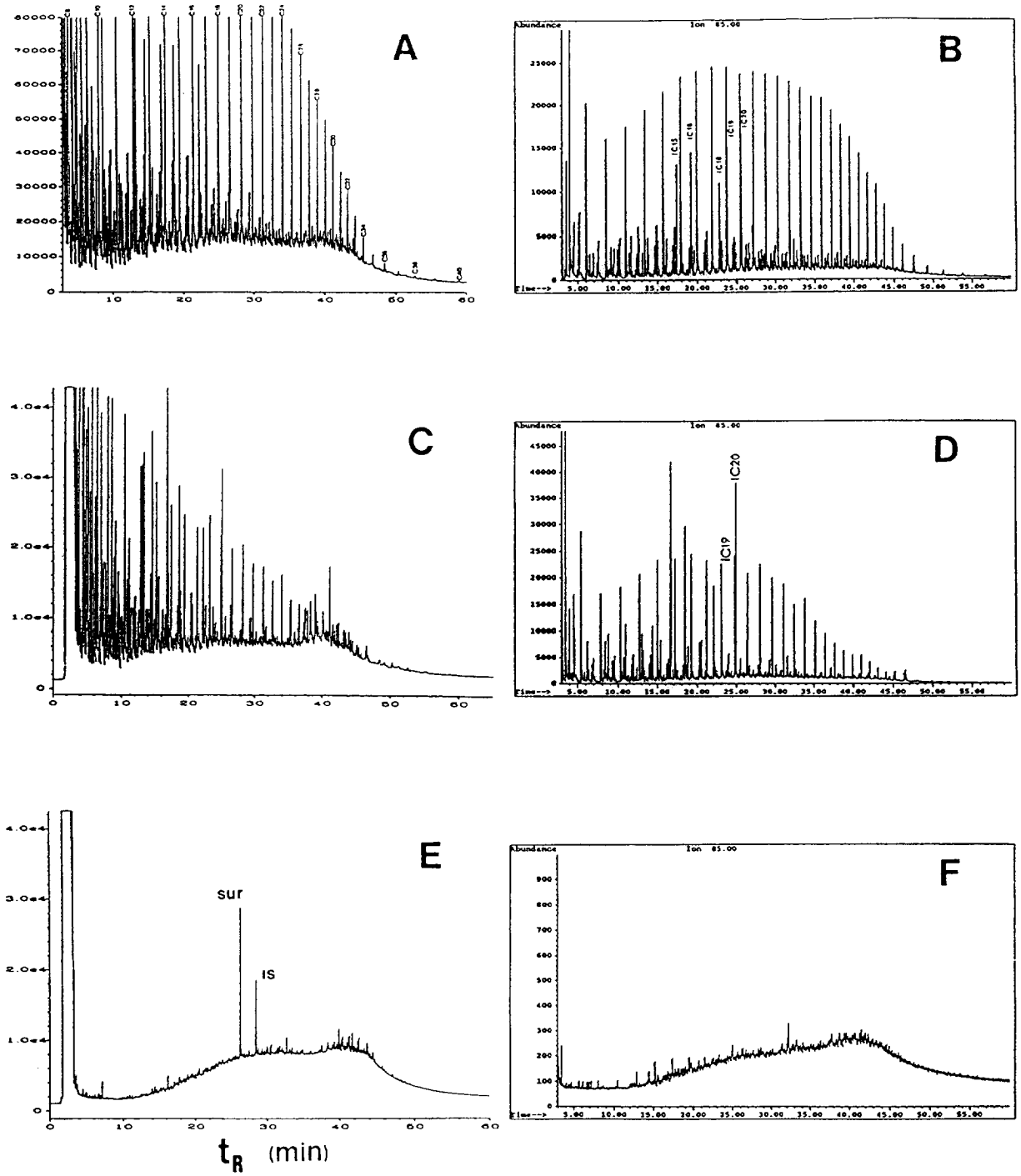

Fig. 1. Comparison of alkane distribution chromatograms (GC–FID and GC–MS at m/z 85) of ASMB oil (A and B), California oil (C and D), and Orimulsion oil (E and F). Numbers represent carbon numbers of n-alkanes.

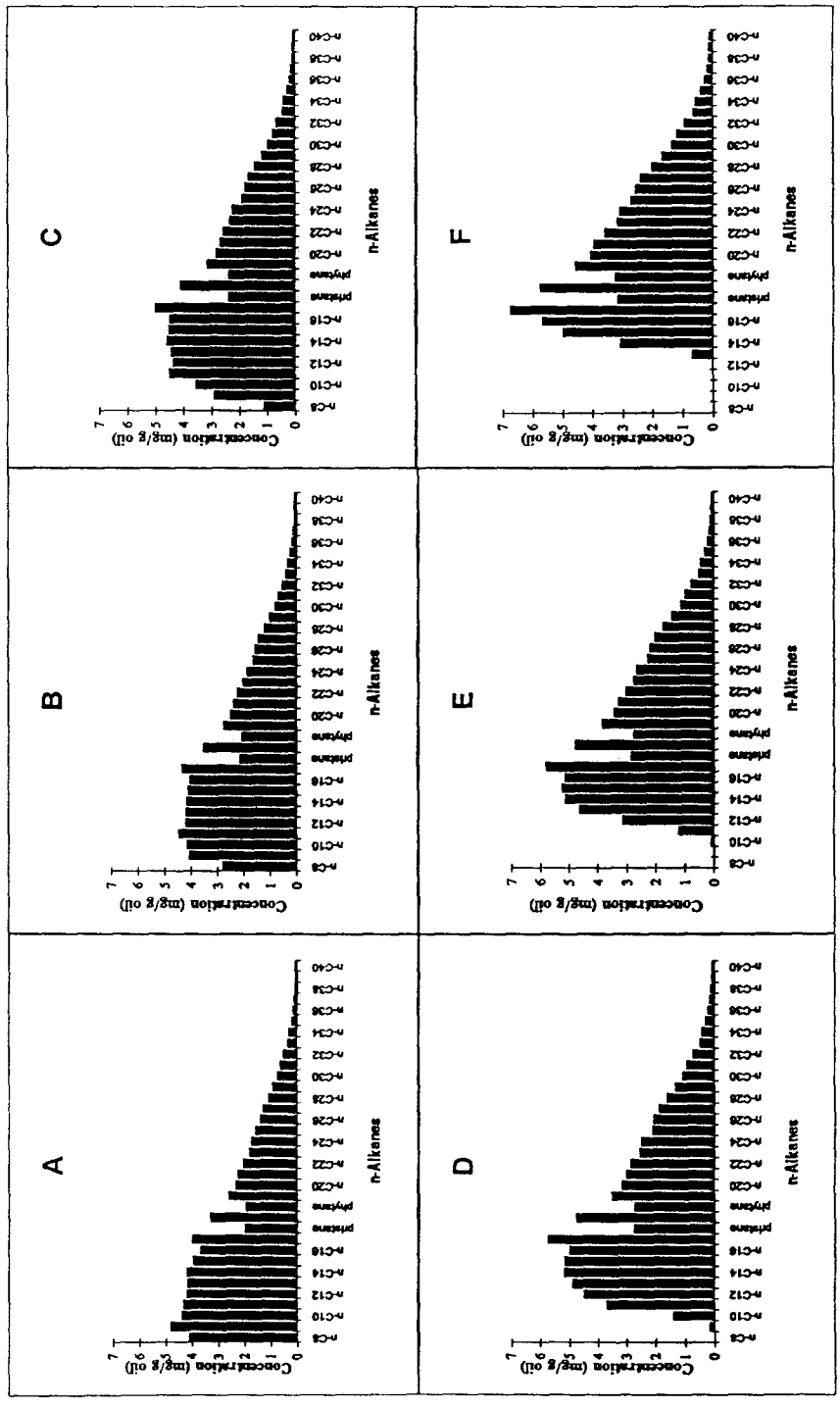

Fig. 2. *n*-Alkane distribution of ASMB oil at six weathering percentages: 0% (A); 9.8% (B); 19.5% (C); 29.8% (D); 34.5% (E); and 44.5 (F).

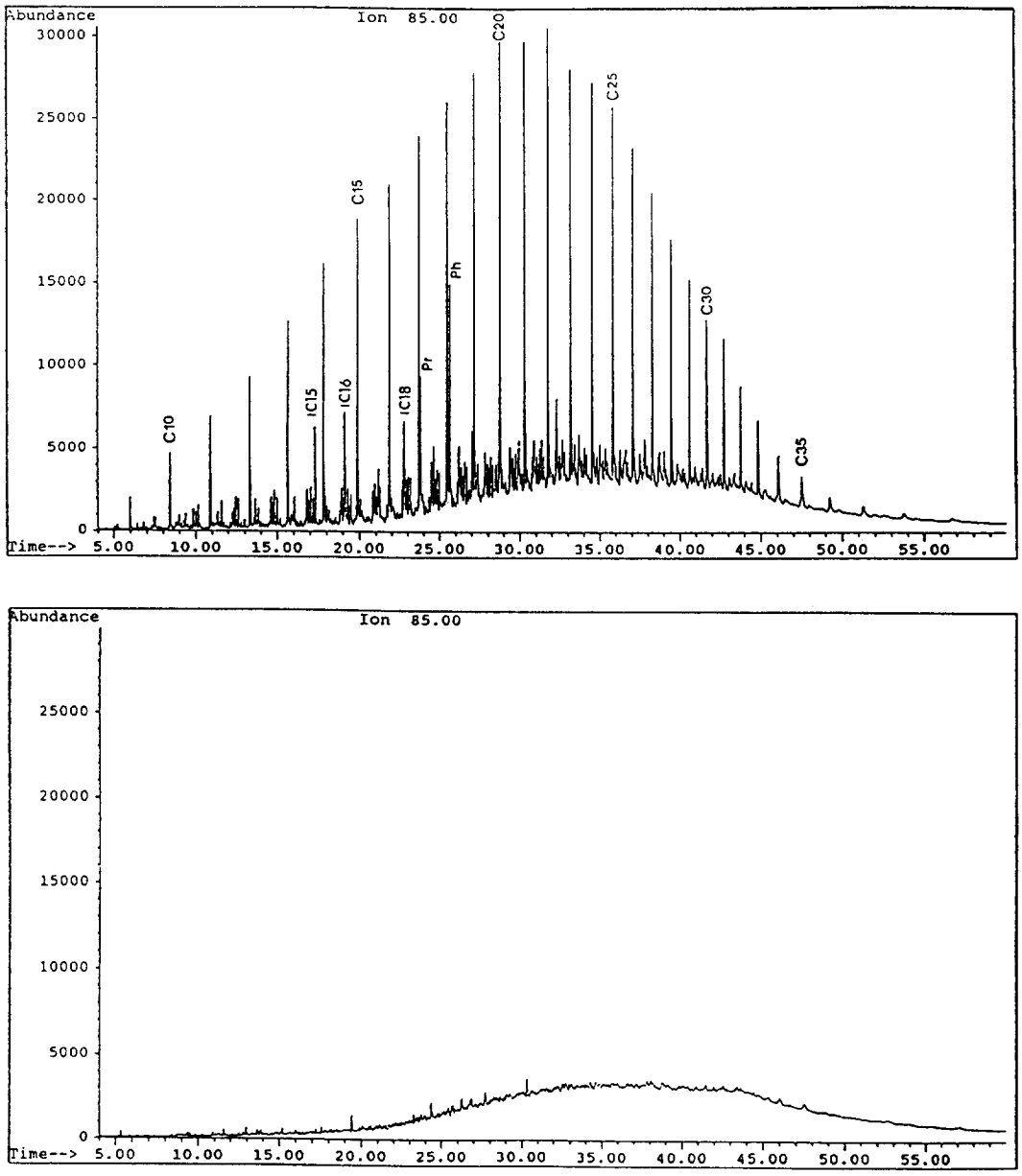

Fig. 3. GC–MS chromatograms of saturated hydrocarbons (m/z 85) for the weathered source Arrow oil (top) and the sample S-4 (bottom). Numbers represent carbon numbers of n-alkanes. iso-C15, iso-C16, iso-C18, Pr, and Ph represent the five most abundant isoprenoids: 2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane, norpristane, pristane, and phytane, respectively.

aromatic compounds) in oil can directly affect the physical and chemical properties of petroleum. The immediate toxic effects of this group of compounds following a spill emphasize the usefulness of analytical data on these groups in biological assessment studies.

The structural identification and characterization of alkyl benzenes are based on mass data in

both scan and SIM modes, comparison of GC retention data with reference standards, and calculation of retention index (I) values verified by comparison with literature I-values. Comparison of the I-values with those reported in the literature enables the assignment of some positional isomers. As an example, Figs. 4A and 4B show the GC–MS scan and SIM chromatograms of alkyl benzene compounds in the retention-time range 2.5–11.5 min obtained from the aromatic fraction of the ASMB oil. Table 2 lists 58 positively identified alkyl benzene compounds with the alkyl group ranging from C_1 to C_8. It is evident from Table 2 that the three series of I-values [the calculated I-values, the literature I-values [17], and the I-values calculated from the chromatographic data of the BTEX and alkyl-benzene (from C_3- to C_6-benzene) standards] are in excellent agreement.

Quantitation of BTEX and alkyl benzenes was achieved by operating GC–MS in the SIM mode and by direct injection of oil in n-pentane solution. It has been noticed that sample handling can greatly affect the analytical precision and accuracy of the determination of alkyl benzene compounds in oil due to the volatility of the lighter alkyl benzenes. In order to achieve improved analytical precision and accuracy, the following refinements were implemented in addition to the routine quality control measures:

(1) Oil was precisely weighed, directly dissolved in n-pentane, and tightly sealed to avoid any possible loss of alkyl benzene compounds, especially the BTEX compounds

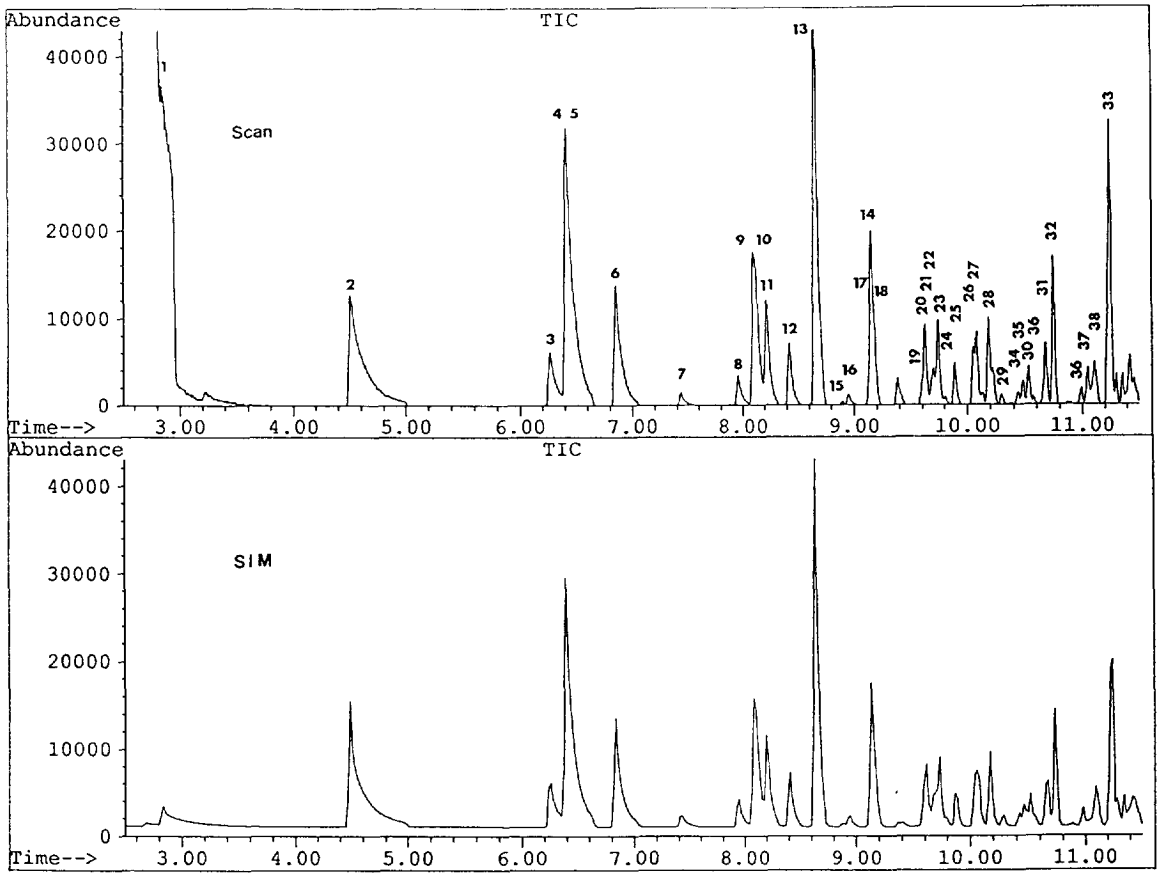

Fig. 4. GC–MS scan (A) and SIM (B) chromatograms of alkyl benzene compounds in the retention time range of 2.5–11.5 min. See Table 2 for component identification.

Table 2
Alkyl-substituted benzene compounds identified in ASMB oil

Peak no.	t_R (min)	Compound identified	M_r	Cal. I	Lit. I	Std. t_R (min)	Std. I
		C0-Benzene					
1	2.840	benzene	78	671.3	670.6	2.836	671.0
		C1-Benzene					
2	4.490	toluene	92	771.2	772.7	4.492	771.3
		C2-Benzene					
3	6.268	ethyl-benzene	106	868.1	867.4	6.264	867.9
4	6.411	*m*-xylene	106	875.3	874.8	6.405	875.0
5	6.421	*p*-xylene	106	875.8	875.4	6.410	875.3
6	6.852	*o*-xylene	106	896.5	898.7	6.847	896.3
		C3-Benzene					
7	7.430	iso-propyl-benzene	120	930.7	931.4	7.437	931.1
8	7.956	propyl-benzene	120	960.7	959.9	7.959	960.8
9	8.080	1-ethyl-3-methyl-benzene	120	967.4	967.2	8.086	967.8
10	8.100	1-ethyl-4-methyl-benzene	120	968.5	969.0	8.096	968.3
11	8.214	1,3,5-trimethyl benzene	120	974.7	974.0	8.214	974.6
12	8.420	1-ethyl-2-methyl-benzene	120	985.5	985.7	8.423	985.7
13	8.653	1,2,4-trimethyl benzene	120	997.5	998.8	8.655	997.6
14	9.137	1,2,3-trimethyl benzene	120	1028.2	>1000	9.135	1028.1
		C4-Benzene					
15	8.886	iso-butyl-benzene	134	1012.1	>1000	8.868	1010.9
16	8.934	*sec.*-butyl-benzene	134	1015.2	>1000	8.920	1014.3
17	9.120	*m*-cymene	134	1027.1		9.122	1027.3
18	9.170	*p*-cymene	134	1030.3		9.162	1029.8
19	9.590	1,3-diethyl-benzene	134	1056.3		9.573	1055.3
20	9.620	1-methyl-3-propyl-benzene	134	1058.1		9.613	1057.7
21	9.674	1-methyl-4-propyl-benzene	134	1061.3		9.685	1062.0
22	9.700	butyl-benzene	134	1062.9		9.710	1063.5
23	9.750	1-ethyl-3,5-dimethyl-benzene	134	1065.9		9.746	1065.6
24	9.800	1,2-diethyl-benzene	134	1068.8		9.793	1068.4
25	9.890	1-methyl-2-propyl-benzene	134	1074.1		9.885	1073.8
26	10.050	1-ethyl-2,4-dimethyl-benzene	134	1083.5		/	/
27	10.080	2-ethyl-1,4-dimethyl-benzene	134	1085.2		10.060	1084.2
28	10.182	4-ethyl-1,2-dimethyl-benzene	134	1091.0		10.188	1091.4
29	10.290	2-ethyl-1,3-dimethyl-benzene	134	1097.1		10.300	1097.7
30	10.528	1-ethyl-2,3-dimethyl-benzene	134	1113.1		10.530	1113.2
31	10.676	1,2,4,5-tetramethyl-benzene	134	1123.2		10.687	1124.0
32	10.745	1,2,3,5-tetramethyl-benzene	134	1127.9		10.725	1126.6
33	11.250	1,2,3,4-tetramethyl-benzene	134	1161.4		/	/
		C5-Benzene					
34	10.430	C5-Benzene	148	1106.3			
35	10.481	C5-Benzene	148	1109.8			
36	10.530	C5-Benzene	148	1114.6			

(*Continued on p. 332*)

Table 2 (*continued*)

Peak no.	t_R (min)	Compound identified	M_r	Cal. *I*	Lit. *I*	Std. t_R (min)	Std. *I*
37	10.992	C5-Benzene	148	1144.5			
38	11.080	C5-Benzene	148	1150.3			
39	11.108	C5-Benzene	148	1154.1			
40	11.230	C5-Benzene	148	1160.1			
41	11.304	amylbenzene	148	1164.9	11.306	1165.0	
42	11.360	C5-Benzene	148	1168.5			
43	11.424	C5-Benzene	148	1172.6			
44	11.458	C5-Benzene	148	1174.8			
45	11.575	C5-Benzene	148	1182.2			
46	11.922	C5-Benzene	148	1204.5			
47	12.101	C5-Benzene	148	1217.6			
48	12.236	C5-Benzene	148	1227.5			
49	13.138	pentamethyl-benzene	148	1290.4	13.133	1290.0	
		C6-Benzene					
50	12.334	C6-Benzene	162	1234.5			
51	12.481	C6-Benzene	162	1245.0			
52	12.579	C6-Benzene	162	1251.9			
53	12.798	*n*-hexyl-benzene	162	1267.2	12.800	1267.3	
54	12.906	C6-Benzene	162	1274.6			
55	13.004	C6-Benzene	162	1281.3			
56	13.053	C6-Benzene	162	1284.6			
		C7-Benzene					
57	14.722	C7-Benzene	176	1408.8			
		C8-Benzene					
58	15.522	C8-Benzene	190	1473.0			

The literature *I*-values listed here are the values after correction of the temperature effect on *I* according to the temperature coefficient given in Ref. [25].

(2) Tightly-capped oil samples were put into a refrigerator to precipitate asphaltenes to the bottom of the vials in order to avoid performance deterioration of the capillary GC column due to the introduction of asphaltenes into the column;

(3) C_3-benzenes in oil were quantitated using the RRFs directly obtained from the respective individual C_3-benzene standards instead of using the RRFs obtained from benzene or C_1/C_2-substituted benzenes.

Individual BTEX compounds and eight C_3-benzene compounds in over 200 oils have been quantified by using the procedures described above. The contents of BTEX and BTEX + C_3-benzenes vary from oil to oil. They can range from 0% up to 6% for BTEX and from 0% up to 7% for BTEX + C_3-benzenes, respectively, depending on the nature and origin of the oil sample. In general, however, the dominance of BTEX and C_3-benzenes in the alkyl-substituted benzene category is obvious.

The loss of BTEX and alkyl benzenes is immediate and significant after an oil spill. It was found that the major changes in alkyl benzene composition on increase of the weathering percentage can be summarized as follows: (1) the rate of loss is significantly correlated to the molecular mass and boiling points of the alkyl benzene compounds. Relative to C_3-benzenes, the low-molecular-mass- and the most volatile BTEX compounds are lost more quickly upon weathering (approximately at weathering percentages of 10–15%, BTEX were nearly com-

pletely lost); (2) the homologous group shows a clear evaporation trend: $C_0 > C_1 > C_2 > C_3 > C_4$; (3) when oil was weathered to approximately 20–25%, the BTEX and C_3-benzenes were completely lost.

3.3. PAHs and their alkylated homologues

PAHs are relatively stable constituents of petroleum and, as from the environmental aspect, they are probably the most important analytes in an oil-spill natural resource damage assessment. As shown in Table 1, the target PAHs and their alkylated homologues include naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene homologous series. Unlike the sixteen EPA-defined priority PAH compounds, these homologous series are very useful in oil-spill assessment, in addition to being essential in evaluating the biological effects. This is because: (1) These alkylated PAH homologues are the most abundant PAH compounds in oil, and they persist for relatively longer periods of time than their parent compounds. Other 4- and 5-ring PAHs are very minor constituents of most crude oils, or are not even detected in many oil samples. (2) Different oils have different distribution profiles of alkylated PAH homologues. They are more valuable than the parent PAHs in fingerprinting the weathered oil, distinguishing between sources of hydrocarbons in the environment, and providing information on the extent and degree of oil weathering and degradation. (3) Reporting values of alkylated PAH homologues more truly reflects the composition of PAHs in oil than using data on parent PAH compounds. The changes in PAH composition caused by weathering and degradation can be more easily detected and traced as well.

Some studies have been performed using distribution of the alkylated PAH homologues as environmental fate indicators and source-specific markers of oil in sediments [12,18,19] and tissue samples [20,21]. Recently, a method using double-ratio plots of alkyl PAH homologues for petroleum source identification has been proposed [12]. This method has been successfully used to correlate the 1989 EXXON VALDEZ spilled-oil sediment samples to the source oil.

Fig. 5A shows the alkylated PAH-homologue distributions in ASMB oil and NOBE oil (Newfoundland Offshore Oil Burn Experiment oil, a type of Alberta oil used specifically for this experiment). For comparison, the abundances of the alkylated PAH homologues were normalized relative to C2-P. These two oils come from very similar origins, but exhibit different PAH signatures, especially the abundances and relative ratios of alkyl dibenzothiophenes. Fig. 5B shows the distribution of alkylated PAH homologues for Bunker C crude. The unusual high abundances of the alkyl phenanthrene series in Bunker C are pronounced. The distinctive

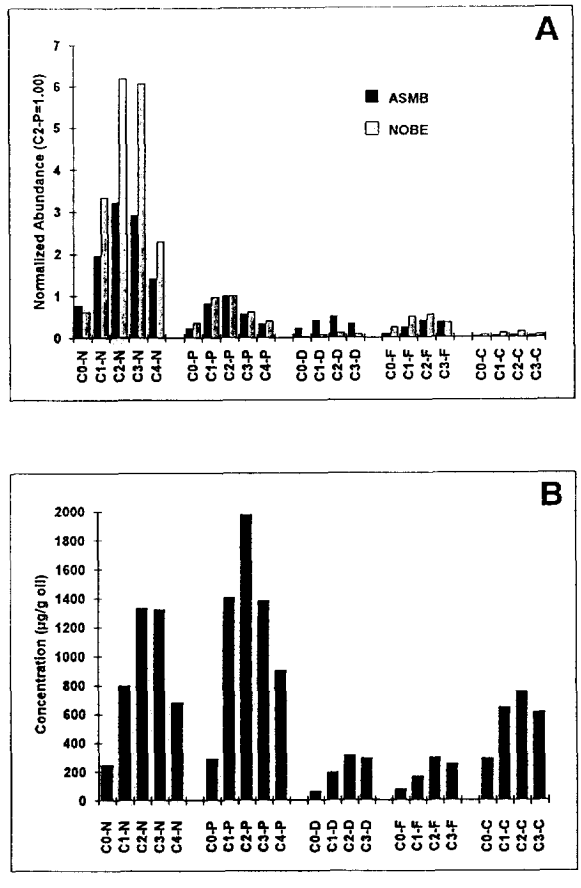

Fig. 5. Alkylated PAH homologous distribution for ASMB oil and NOBE oil (normalized abundance: C2-P = 1.00, A), and for Bunker oil (B).

character of each oil, as evidenced by the alkylated PAH-homologue distributions, is apparent. If only the 16 priority PAH compounds were the target analytes, such differences of composition between two oils would not be evident.

Fig. 6A–C shows the GC–SIM-MS chromatograms of the aromatic compounds of ASMB oil

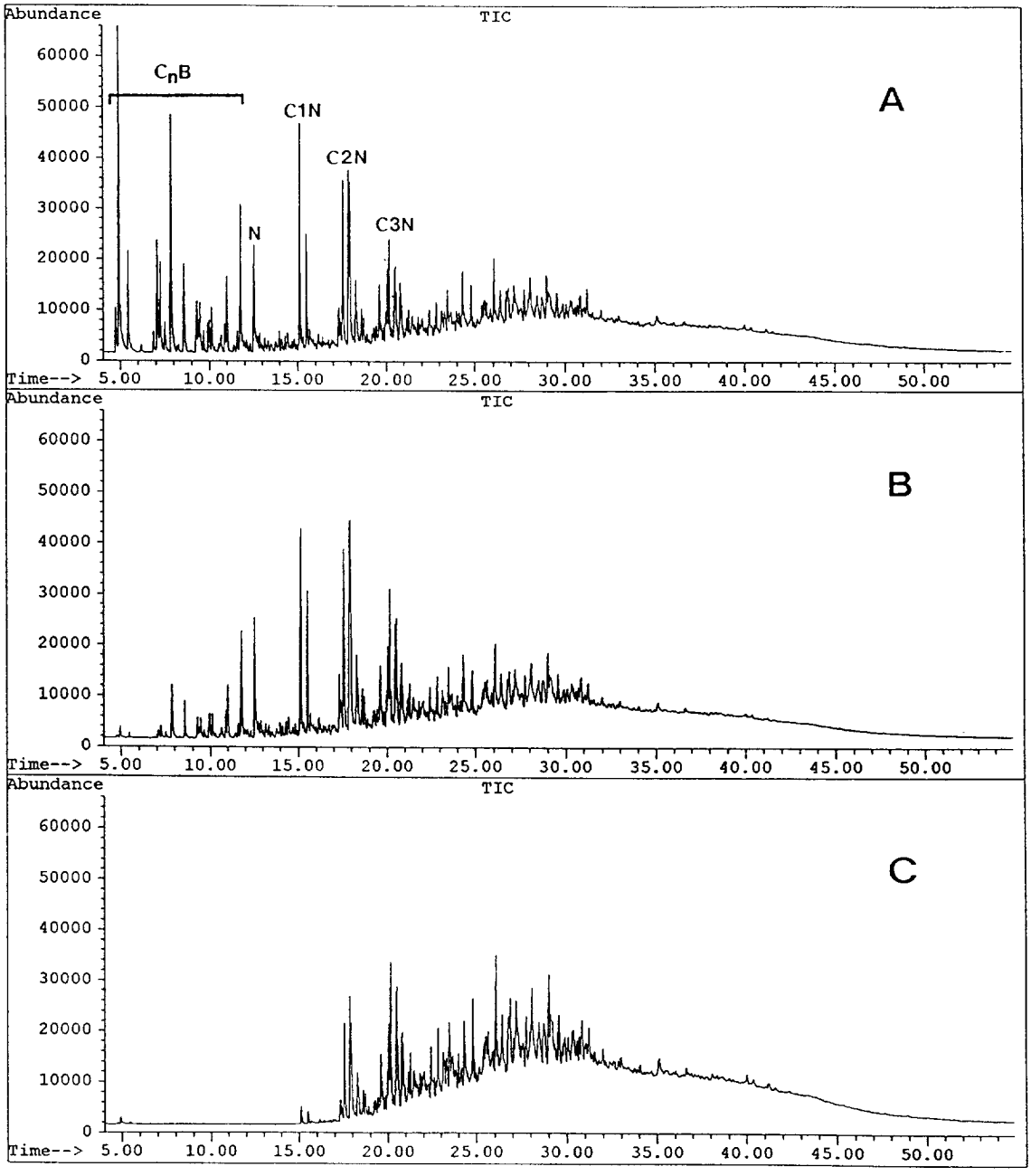

Fig. 6. GC–MS chromatograms of aromatic compounds of ASMB oil at weathering percentages 0% (A), 29.8% (B), and 44.5% (C). CnB, N, C1N, C2N, and C3N represent alkyl benzenes, naphthalene, and alkylated naphthalenes, respectively.

samples at 0%, 29.8%, and 45% artificially weathered (by evaporation). The loss of low-boiling alkyl benzenes and alkylated naphthalene homologues is very apparent as weathering increase. Fig. 7 shows the alkylated-PAH fingerprints of weathered Arrow oil, and three 22-year-old spilled Arrow oil samples S-6, S-A and S-9, showing the preferential loss of certain alkylated PAH homologues in highly-weathered Arrow oil samples and illustrating the effect of field weathering on PAH composition [in order to clearly show the changes in the distribution patterns within the different PAH families, different scales for y-axis were applied to Fig. 7A (0–3200 μg/g TSEM), 7B (0–800 μg/g TSEM), 7C and 7D (0–400 μg/g TSEM), respectively]. Conducting such analyses over time and at different locations with different exposures will provide essential information on the long-term impact of spilled oil on the environment.

It has been demonstrated [6] that the ratios for PAH compounds within an isomer group are relatively consistent even after evaporation. However, if any biodegradation occurs, the ratios of the isomers change within the same isomeric group [15,16]. Fig. 8A–E shows GC–

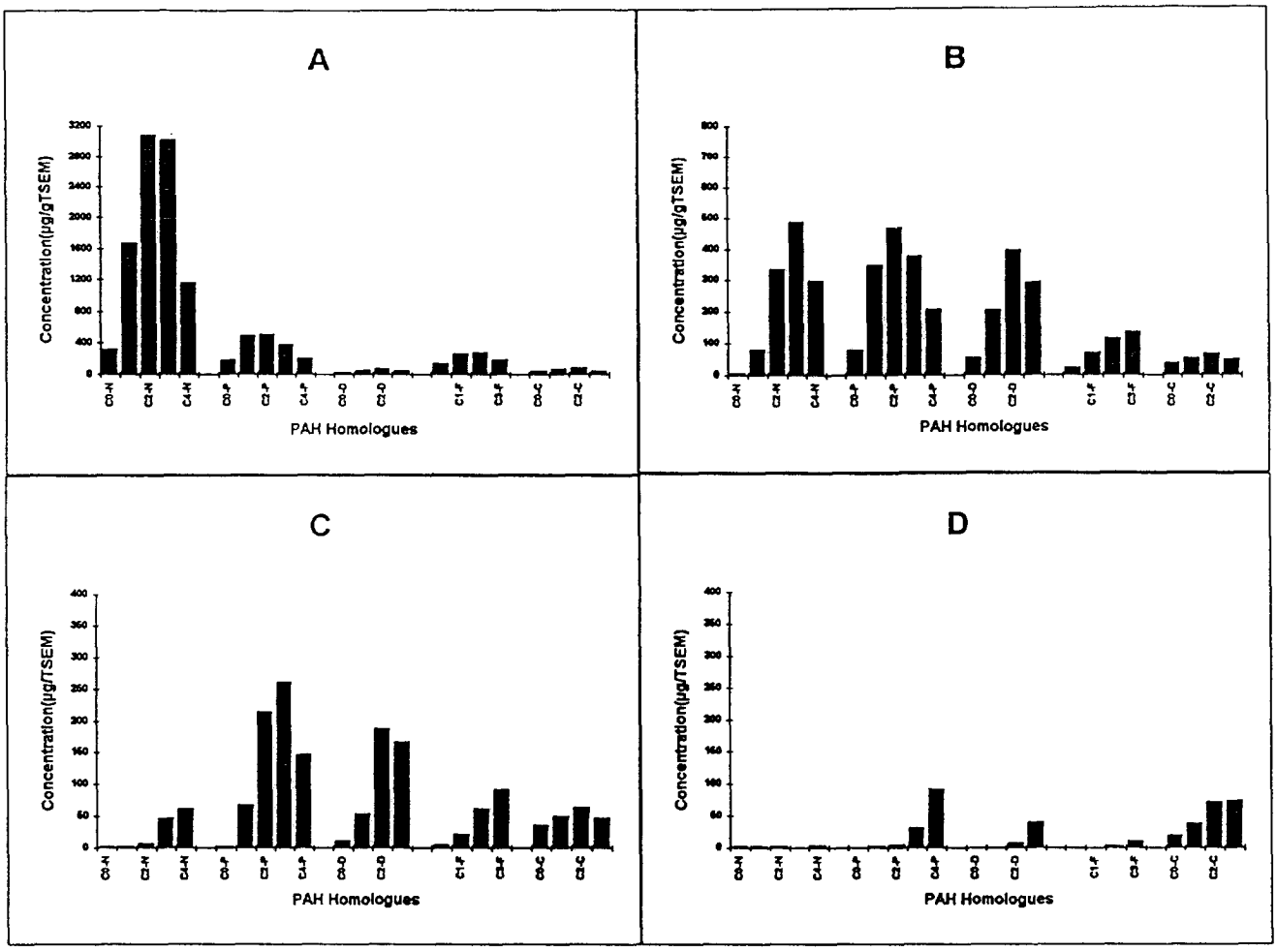

Fig. 7. Alkylated PAH fingerprints of the weathered source oil (A), samples S-6 (B), S-A (C), and S-9 (D) illustrating the effects of weathering on PAH compositions. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0, 1, 2, 3, and 4 represent carbon numbers of alkyl groups in alkylated PAH homologoues.

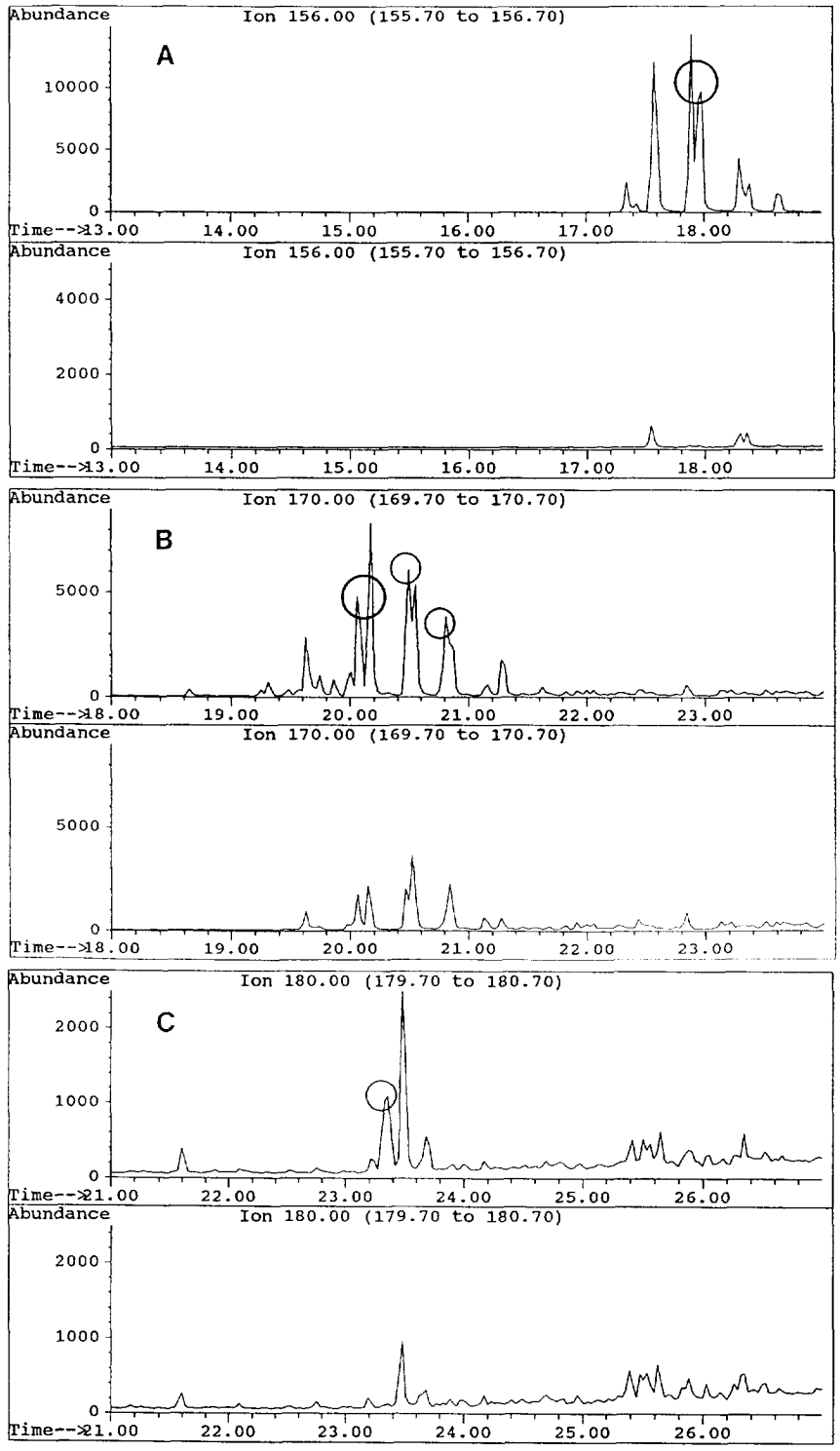

Fig. 8. Extracted ion chromatograms for C_2-naphthalenes (*m/z* 156, A), C_3-naphtalenes (*m/z* 170, B), C_1-fluorenes (*m/z* 180, C), C_1-phenanthrenes (*m/z* 192, D), and C_1-dibenzothiophenes (*m/z* 198, E) in the source ASMB oil and corresponding biodegradation ASMB oil samples. The circled regions show the changes in distribution among isomers that were preferentially degraded by bacteria.

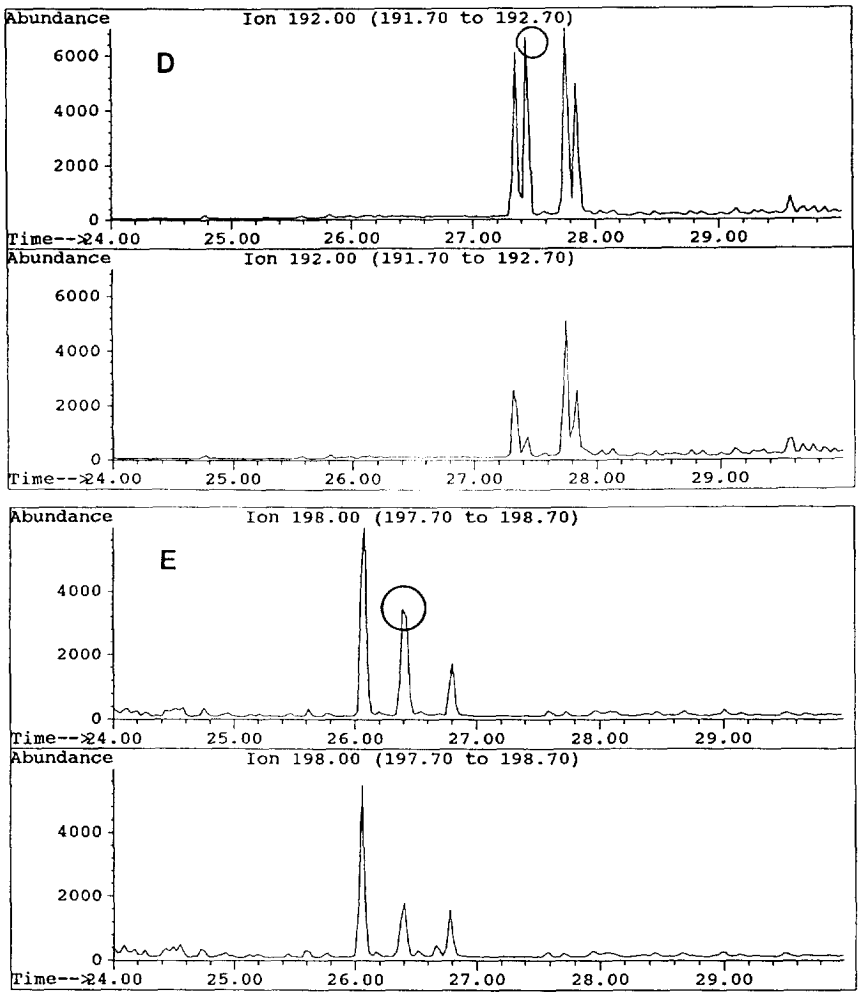

Fig. 8 (*continued*).

MS fragmentograms of C_2-naphthalenes (m/z 156), C_3-naphthalenes (m/z 170), C_1-fluorenes (m/z 180), C_1-phenanthrenes (m/z 192), and C_1-dibenzothiophenes (m/z 198) in the source ASMB oil and the biodegradated oil samples incubated for 28 days at 4°C with cold marine standard inoculum. The circled regions in Fig. 8 show the changes in distribution among isomers that were selectively altered by biodegradation. It can be seen from Fig. 8 that among six identified C_2-naphthalenes (Fig. 8A: ethyl-, 2,6-, 1,3-, 1,6-, 2,3-, and 1,2-dimethyl-naphthalene), eight identified C_3-naphthalenes (Fig. 8B: $\beta\beta$-ethylmethyl-, $\alpha\beta$-ethylmethyl-, 1,3,7-, 1,3,6-, 1,3,5-, 2,3,6-, 2,3,5-, 1,2,7-, 1,2,5-trimethyl-naphthalene), three identified C_1-methyl-fluorenes (Fig. 8C: methyl-, 2-, and 1-methyl-fluorene), four identified C_1-phenanthrenes (Fig. 8D: 3-, 2-, 4-/9-, and 1-methyl-phenanthrene), and three identified C_1-dibenzothiophenes (Fig. 8E: 4-, 2-/3-, and 1-methyl-dibenzothiophene), bacteria most preferentially degraded 1,3- and 1,6-dimethyl-naphthalene, 1,3,7-, 1,3,6-, 1,3,5-, and 2,3,5-trimethyl-naphthalene, methyl-fluorene, 2-methyl-phenanthrene, and 2-/3-methyl-dibenzothiophene. This finding has great importance because the ratios within the isomeric PAH groups can be used as markers of biodegradation. The concentrations and relative distributions among and between isomers of

alkyl homologue groups from hundreds of biodegradation samples have been calculated. Evaluation of the data results in a qualitative determination of the extent and progress of biodegradation in the samples. These qualitative data, when used in conjunction with quantitative data on the changes in distribution of the entire PAH homologous groups, may be used to evaluate the effects of bioremediation products on oil degradation.

3.4. Biomarker compounds

For decades triterpanes and steranes have been used as biomarker compounds for the identification of petroleum deposits by petroleum geochemists [22–29]. These biomarkers were later used for oil fingerprinting by environmental chemists to study the fate and to trace the source of spilled oil [30–35]. Analysis of biomarker compounds offers several distinct advantages: (1) triterpanes and steranes are unique for each oil. The distribution patterns of biomarker compounds, in general, are different from oil to oil. Therefore they are useful in identification of the oil source; (2) they are highly degradation-resistant compounds in comparison to the aliphatic and aromatic compounds. As an oil becomes more degraded the concentration of biomarker compounds should increase relative to the more easily degraded constituents; (3) calculation based on hopane analysis to estimate percent of oil depletion can provide a more accurate representation of the degree of oil degradation than the traditional aliphatic/isoprenoid hydrocarbon ratio, and can greatly improve the ability to resolve biodegradation differences between sites.

Fig. 9A–F shows hopane and sterane distribution chromatograms of three crude oils (ASMB oil, NOBE oil, and California oil). ASMB oil and NOBE oil are of similar origins and both are light oils. California oil is much heavier than ASMB oil and NOBE oil (the API gravity for California oil and ASMB oil is 15 and 37, respectively). Even by visual comparison, these three oils can be readily distinguished by the distribution profiles and the relative amount of hopanes and steranes. Analysis of several hundreds of different oils and spilled-oil samples demonstrates that triterpane compounds in oils are distributed in a wide range from C_{19} to C_{35} with various pentacyclic hopanes (such as C_{29}-$\alpha\beta$- and C_{30}-$\alpha\beta$-hopane, peaks 17 and 19 in Fig. 9A) being prominent. In the distribution of steranes, the dominance of C_{27}, C_{28}, and C_{29} steranes (peaks 42 through 53 in Fig. 9B) is apparent for most oils. A significant contribution from the diasteranes is also observed for some oils.

A lightly degraded oil is usually indicated by partial depletion of *n*-alkanes; a moderately-degraded one is often indicated by heavy loss of *n*-alkanes and partial loss of lighter PAH compounds. However, from extensively degraded oil samples [such as 22-year-old Arrow oil samples and heavily-weathered Baffin Island Oil Spill (BIOS) samples], the *n*-alkanes and branched alkanes might have been completely lost, and PAHs and their alkyl homologues could be highly degraded. In such cases, identification through recognition of *n*-alkanes and/or PAH distribution pattern would be rather difficult, and analysis of biomarker compounds would be not only necessary but also particularly important and valuable, because only these highly degradation-resistant compounds remain in the samples after long-term weathering and can give chemical "fingerprinting" information of the source, degree of weathering, characteristics and fate of the spilled oil.

Two criteria are used for matching the long-term weathered oil with the source oil: (1) whether the distribution profile and pattern of the *m/z* 191 and 217 fragments are the same; (2) whether the computed ratios of some target pairs of terpane and sterane compounds are near identical. Table 3 lists and compares some diagnostic ratios from two groups of highly-weathered and degraded oil samples (Arrow and BIOS). Due to the extensive weathering, the Arrow oil samples were characterized by the total loss of *n*-alkanes and isoprenoids and heavy loss of PAH compounds, resulting in the traditional *n*-alkane/isoprenoid ratios being non-calculable. The double ratios of some remaining

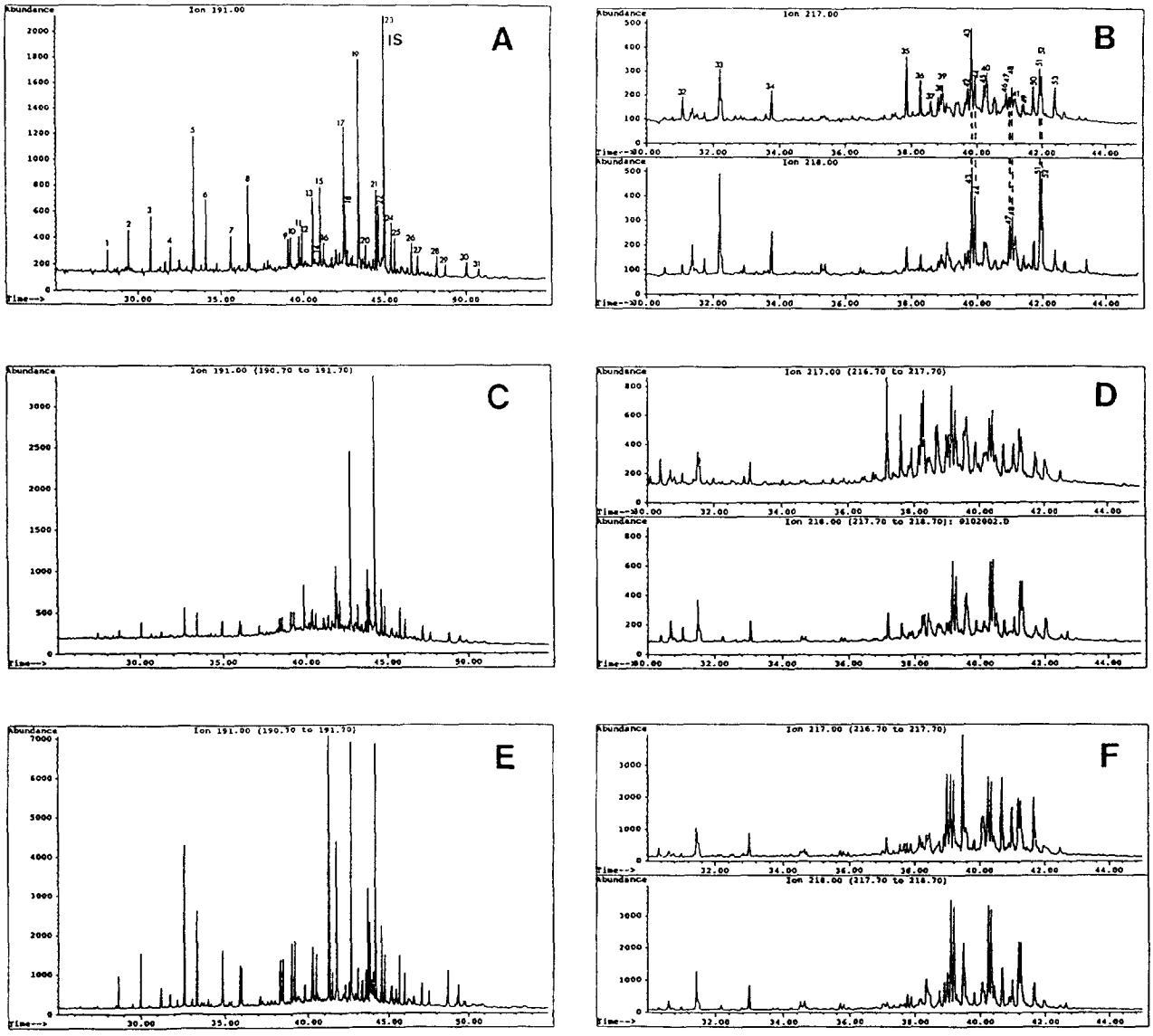

Fig. 9. Distribution of hopanes (m/z 191) and steranes (m/z 217 and 218) in ASMB oil (A and B), NOBE oil (C and D), and California oil (E and F).

PAH homologues (C_2D/C_2P and C_3D/C_3P) did not show any clear correlation between samples either. Less weathered BIOS samples showed similar results except that n-alkanes and isoprenoids were only partially lost and the ratios of pristane/phytane showed some correlation between samples. Fortunately, however, the GC–MS measurements demonstrate that the profiles and patterns of the m/z 191 and 217 ion chromatograms of the Arrow oil and BIOS samples are nearly identical, except that a few samples (such as S-1 and S-10) showed the similar distribution patterns but with some peaks being less abundant and even undetectable. More importantly, the computed ratios of target hopane compounds (C_{29}/C_{30}) appear to be consistent for all samples (0.86 and 0.95 for Arrow and BIOS series, respectively) and, therefore, can be

Table 3
Comparison of diagnostic ratios for Arrow and BIOS samples

Sample	Weathered source oil	Arrow oil samples										
		S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-A
C17/pristane	1.66	non-calculable					1.37	non-calculable				
C18/phytane	1.47	non-calculable					1.00	non-calculable				
pristane/phytane	0.87	non-calculable					0.75	non-calculable				
C2D/C2P	0.85	0.22	1.80	0.85	0.98	1.20	0.85	0.79	2.40	1.90	0.65	0.88
C3D/C3P	0.78	0.60	1.40	0.67	0.83	1.10	0.77	0.95	0.96	1.30	0.65	0.64
C23/C24	2.07	0.62	2.05	2.06	2.07	2.10	2.06	2.09	2.07	1.98	1.00	2.05
Ts/Tm	0.26	0.31	0.28	0.26	0.27	0.27	0.26	0.27	0.28	0.29	0.36	0.27
C29/C30	0.86	0.87	0.84	0.86	0.86	0.87	0.86	0.87	0.86	0.86	0.89	0.86
		BIOS oil samples										
		BIOS-1	BIOS-2	BIOS-3	BIOS-4	BIOS-5	BIOS-6	BIOS-7	BIOS-8	BIOS-9	BIOS-10	BIOS-11
C17/pristane	3.44	2.20	0.00	0.90	1.16	0.76	0.90	0.16	2.25	2.42	2.29	0.19
C18/phytane	1.47	1.05	0.00	0.77	0.51	0.31	0.42	0.13	1.03	1.01	1.04	0.14
pristane/phytane	0.53	0.55	0.32	1.09	0.54	0.41	0.40	0.26	0.54	0.55	0.51	0.54
C2D/C2P	1.10	1.78	1.33	0.71	1.06	1.11	0.87	1.20	2.24	0.13	1.87	1.52
C3D/C3P	0.91	1.15	1.03	0.74	0.95	1.09	0.84	1.05	1.08	0.24	1.29	1.02
C23/C24	2.17	2.18	2.15	1.53	2.14	1.94	1.61	2.02	2.12	2.14	2.16	2.16
Ts/Tm	0.22	0.24	0.23	0.22	0.24	0.28	0.33	0.27	0.23	0.24	0.24	0.23
C29/C30	0.95	0.95	0.93	0.94	0.95	0.95	0.94	0.95	0.95	0.95	0.96	0.94

used as a good indicator for oil identification. Besides that, the relatively lower abundant, but well-resolved, paired C_{32} and C_{33} 22*S*/22*R* hopane isomers (peaks 24 through 27 in Fig. 9A) also show very good consistency in the values of $22S/(22S + 22R)$ ratios for each series of samples.

It is noticed that for most of the Arrow and BIOS samples the ratios of paired terpanes Ts/Tm (Ts: 18α(H),21β(H)-22,29,30-trisnorhopane; Tm: 17α(H),21β(H)-22,29,30-trisnorhopane; peak 13 and 15 in Fig. 9A) and C_{23}/C_{24} (peaks 5 and 6 in Fig. 9A) are also quite consistent, but for samples S-1 and S-10, BIOS no. 5, no. 6, and no. 7, much lower C_{23}/C_{24} values and higher Ts/Tm values were observed. The ratio of the C_{27} pentacyclic terpanes Ts and Tm has been used as a geochemical parameter to characterize both source input and maturity of a crude [36] and as an indicator for oil matching [8,37]. In most cases, Ts and Tm were apparently independent of weathering effect and therefore can be useful in matching of oils. However, this does not hold for those residual oils in sediments which have undergone long-term extensive weathering and biodegradation, as in the case of samples S-1 and S-10, and nos. 5, 6 and 7. As shown in Table 3, the ratios of Ts/Tm increased from a value around 0.27 for most Arrow samples and 0.23 for most BIOS samples to 0.31, 0.36, 0.28, 0.33 and 0.27 for these five samples, respectively. It has been reported [37] that as maturation takes place either in the kerogen matrix or in the reservoir on a geological time scale, Tm shows a relatively faster rate of depletion than Ts. This study also demonstrated that Tm has a relatively faster rate of biodegradation than Ts (even though Ts chromatographically elutes earlier than Tm), resulting in higher Ts/Tm ratios for those very

Table 4
Quantitation of TSEM, TPH, *n*-alkanes, PAHs, and selected paired hopane isomers, and estimation of weathering percentages of oil in BIOS samples

Sample	Quantitation of hydrocarbons				Target hopanes (μg/g TSEM)				Weathering perentages (%)		
	TSEM (mg/g of sample)	TPH by GC (mg/g of sample)	Total *n*-alkanes (mg/g TSEM)	Alkylated PAHs (mg/g TSEM)	C23 (μg/g TSEM)	C24 (μg/g TSEM)	C29 aβ (μg/g TSEM)	C30 aβ (μg/g TSEM)	Based on C29 hopane	Based on C30 hopane	Average
BIOS-1	36.3	17.9	44.3	3.0	163	75	129	136	10.1	10.3	10
BIOS-2	9.3	3.4	1.40	3.9	174	81	145	157	20.0	22.3	21
BIOS-3	0.0115	0.0014	7.17	0.41	109	72	131	139	11.5	12.2	12
BIOS-4	29.9	13.4	27.9	4.1	179	84	145	153	20.0	20.3	20
BIOS-5	0.169	0.042	4.97	0.49	267	138	287	303	60.0	60.0	60
BIOS-6	0.0807	0.0164	4.36	0.22	185	116	289	308	60.0	60.4	60
BIOS-7	0.55	0.15	7.11	0.47	222	109	221	231	47.5	47.2	47
BIOS-8	4.0	2.1	44.4	3.5	166	78	136	143	14.7	14.7	15
BIOS-9	19.3	10.4	41.2	2.4	158	74	126	132	8.0	7.6	8
BIOS-10	33.3	15.1	39.7	1.8	166	77	132	138	12.1	11.6	12
BIOS-11	15.1	7.4	13.3	4.5	180	83	150	160	22.7	23.8	23
Weathered source oil	868	530	56.0	8.0	156	72	125	131	7.2	6.9	7
"Fresh" source oil					142	65	116	122			

heavily biodegraded samples. The same hold for C_{23}/C_{24}. Both of these two relatively small terpanes are biodegradable, but with the degradation rate of C_{23} being faster than that of C_{24}, resulting in lower C_{23}/C_{24} ratios.

As shown in Table 3, the combined ratios of the selected pairs of terpanes, especially the ratio of C_{29}/C_{30} hopane, are apparently independent of weathering effects and can be useful in identification of oil source and in oil matching. It should be understood, however, that there is no single ratio which can be used to positively identify the source of an unknown spilled oil by itself without matching it to known oils. Other diagnostic ratios (such as those obtained from *n*-alkanes and alkylated PAH homologues) remain necessary and useful for oil source identification and characterization.

A method based on biomarker compounds (using C_{29}-$\alpha\beta$- and C_{30}-$\alpha\beta$-hopane as internal oil references) to estimate oil weathering percentages in environmental samples has been developed and successfully used for determination of weathering percentages of oil in BIOS samples using the following equation [6,9,32]:

$$P(\%) = (1 - C_s/C_w) \times 100(\%)$$

where P is the weathering percentage of the weathered samples; C_s is the concentration of C_{29}-$\alpha\beta$- and C_{30}-$\alpha\beta$-hopane in the source BIOS oil; C_w is the concentration of C_{29}-$\alpha\beta$- and C_{30}-$\alpha\beta$-hopane in the weathered BIOS samples.

The results in Table 4 show that the BIOS samples nos. 1, 4, 8, 9, and 10 were less weathered with weathering percentages in the range 8–20%, while the weathering percentages for the highly weathered samples nos. 5, 6, and 7 were determined to be as high as 50–60%. These results show excellent correlation to the TSEM (total solvent extractable materials), TPH (total petroleum hydrocarbons by GC), aliphatic, PAH, and biomarker compound analysis results. For example, the samples nos. 5, 6, and 7 with the highest weathering percentages showed the lowest TSEM and TPH values, the lowest concentrations of *n*-alkanes and alkylated PAH homologues, the highest concentrations of hopanes (Table 4), while the samples with the lowest weathering percentages, nos. 1, 4, 8, 9, and 10, demonstrated the reverse trends.

4. Conclusions

This paper described a high-performance capillary gas chromatographic–mass spectrometric technique for the determination of individual petroleum hydrocarbon compounds and specific compound types and classes including C_8 through C_{40} normal alkanes, the isoprenoids pristane and phytane, BTEX and alkyl benzenes, target polycyclic aromatic hydrocarbons and their alkylated homologues, and biomarker triterpanes and steranes. The analytical methods described for the determination of target hydrocarbons in crude oil, weathered oil, spilled oil and oil-spill-related environmental samples are more selective and more representative of the true composition of oil, and hence more defensible than some other traditional methods which were originally designed for industrial waste and hazardous waste. 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. In addition, the present work also demonstrated that the efficient oil source identification and estimation of weathering percentages for very heavily weathered oil samples can be accomplished by the selective use of biomarker parameters.

It should be noted that although the GC–MS techniques described provide an increase in hydrocarbon fingerprint resolution, other analytical approaches remain necessary, and are complementary to the GC–MS techniques.

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