10 Chemical Heterogeneity in Modern Marine Residual Fuel Oils

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10.1 Introduction

The vast majority of the vessels that make up the more than 700 million dry weight tonnes of the world's merchant marine fleet are powered by massive marine diesel engines that operate on heavy marine fuel oils derived from residual oil (Hiedeloff and Stockmann, 2005). In the maritime industry, ship fuels are commonly referred to as "bunker fuels" — derived from the notion than these fuels are stored in ships' holds that, during the coal-propulsion shipping era, were referred to as bunkers. Both routine commercial shipping operations (e.g., fueling and bilging) and maritime accidents (e.g., groundings, collisions, or sinking attributable to foul weather or mechanical failures) can lead to the operational discharge or accidental spillage of marine fuel oil, being carried as both fuel and cargo, into the sea. Annual estimates of petroleum discharged or spilled into the sea by worldwide commercial vessel operations approach 1 million tonnes (NRC, 2003). In the case of catastrophic maritime accidents involving commercial cargo vessels, many tens to hundreds of tons of fuel oil can be lost to the sea virtually at once, or chronically over days or months after an accident.

Oil spill investigators are often called upon to determine the source and fate of oil spilled in the sea. In some cases, investigators are asked to determine the likely source of "mystery" spills of oil found in shipping lanes, harbors, or the open ocean. In cases involving catastrophic spills of oil, investigators need to track the spilled oil in the environment and, ultimately, to differentiate that oil from other sources of fugitive petroleum in the environment (Stout et al., 2005; Hendrick and Reilly, 1993).

Because of their preponderant use as fuel in marine vessels, marine residual fuels are often the focus of maritime oil spill investigations. Residual fuels, often referred to generically as heavy fuel oil or HFO, pose a variety of challenges to oil spill investigators: from a fate and transport perspective, heavy fuel oils are typically low API gravity, with densities approaching, and sometimes exceeding, that of water (Neff et al., 2003; National Academy of Sciences, 1999). As such, heavy fuels may float on water, sink, or alternatively sink and then resurface, depending on meteorologic conditions (NOAA, 1997; Michele and Galt, 1995).

Heavy fuel oils are also distinctive in terms of their refining and production history. In fact, variability in the composition of modern heavy marine fuels provides unique opportunities for chemical "fingerprinting" of HFOs in the environment. In this chapter, we focus on the forensic chemistry of HFO — the most widely used of the commercial marine fuel oils — and chemical features of these fuels pertinent to oil spill investigations. A brief history of HFO production, use, and classification is presented. Distinctive chemical features of heavy fuels are described. The results of detailed chemical analyses for 71 modern worldwide IFO 380 HFOs are offered to demonstrate the variability in the composition of marine residual fuel oils.

10.1.1 Historical Perspective

The use of petroleum for ship propulsion began in the late 19th century, shortly after the discovery and production of commercially available petroleum. By the early 20th century, most commercial ships had converted from coal to oil-fired steam boiler propulsion plants. During the first half of the 20th century, the maritime propulsion fuel of choice was distillate-based; however, as the demand for distillate fuel and automotive gasoline grew, there was a strong economic incentive for maritime ship operators to develop boilers and diesel engines capable of burning cheaper fuels derived from less valuable refining residuals (Newbery, 1996). By the late 1950s, a majority of commercial ships were propelled by diesel engines fired by residual fuels, or so-called heavy fuel oils (HFOs). Until the Middle Eastern oil embargos of the early and mid-1970s, the consistency and quality of these vintage heavy fuels were, by all accounts, reasonable and predictable. These early HFOs were derived from the relatively simple residuals of atmospheric and vacuum distillation of crude oil.

In the wake of the 1970s oil embargos, worldwide petroleum refiners were forced to better utilize residual stocks to produce more distillate and automotive gasoline through more aggressive, complex refining — typically involving additional thermal and catalytic cracking processes. The quality of the cracked residuums resulting from these advanced refining processes varied, but in general were poorer quality than straight-run atmospheric or vacuum-distilled residuals. The viscosity of the cracked residuums increased, and the concentrations of undesirable constituents like sulfur, metals, and inorganic residues were greater than in simpler straight-run residuals. To achieve the performance specifications demanded by the marine heavy fuel market, refiners began blending and reformulating poor-quality cracked residuums with products such as cracked gas oils and other available refinery intermediates, so the resulting heavy fuel oils could be burned in modern marine diesel engines (Newbery, 1996; Winkler, 2003). Coincidently, maritime engineers improved marine diesel engines to reliably burn more chemically and physically diverse heavy fuel oils formulated from cracked, heavy residual blends.

10.1.2 Production of Heavy Fuel Oils

Heavy fuel oils are produced from residuals — the “leftovers” from the crude oil refining process (Leffler, 2000). As mentioned earlier, until the early 1970s, this primarily included the nondistillable residuum from the atmospheric distillation process (i.e., the fraction of crude oil that did not boil above 1050°F to 1100°F). Today, however, most refiners also utilize vacuum distillation techniques that “squeeze” even more desirable, lighter products from atmospheric distillation residuum. The residuum from vacuum distillation, often termed “flasher bottoms,” is the primary feedstock in the current production of modern heavy fuel oils (HFOs). As the sophistication of the refining process increased to include additional steps aimed at squeezing more profit from residuums (e.g., thermal and catalytic cracking, visbreaking, coking), smaller volumes and lower-quality cracked HFO feedstocks resulted. Lower quality is typically expressed in terms of higher concentrations of sulfur, ash (sometimes associated with catalyst fines), and metals, and higher viscosity, pour point, and water content.

The reduction in the quality of residual fuel feedstocks has led to the need to blend other lower boiling residuals (e.g., cat-cracked gas oil), with the heavy distillation residuals in order to achieve HFO specifications. Though considered controversial, it has not been uncommon for producers of HFOs to use small amounts of used automotive and crankcase lubricating oil as a blending stock for residual fuels as a means of disposal (Mazur et al., 2004). Interestingly, only the most recent revisions of the ISO specifications for marine fuels expressly prohibit the use of lubricating oil (ULO) as blending components to marine fuels (ISO, 2005).

Table 10-1 ISO Specifications for Marine Residual Fuel Oils[1]

Parameter	*Unit*	*Limit*	*RMA 30*	*RMB 30*	*RMD 80*	*RME 180*	*RMF 180*	*RMG 380*	*RMH 380*	*RMK 380*	*RMH 700*	*RMK 700*
Density at 15°C	kg/m^3	Max	960	975	980	991		991		1010	991	1010
Viscosity at 50°C	mm^2/s	Max	30		80	180		380			700	
Water	% V/V	Max	0.5		0.5	0.5		0.5			0.5	
Microcarbon Residue	% m/m	Max	10		14	15	20	18	22		22	
Sulfur[2]	% m/m	Max	3.5		4	4.5		4.5			4.5	
Ash	% m/m	Max	0.1		0.1	0.1	0.15	0.15	0.15		0.15	
Vanadium	mg/kg	Max	150		350	200	500	300	600		600	
Flash point	°C	Min	60		60	60		60			60	
Pour point, Summer	°C	Max	6	24	30	30		30			30	
Pour point, Winter	°C	Max	0	24	30	30		30			30	
Aluminum + Silicon	mg/kg	Max	80		80	80		80			80	
Total Sediment, Potential	% m/m	Max	0.1		0.1	0.1		0.1			0.1	
Zinc[3]	mg/kg	Max	15									
Phosphorus[3]	mg/kg	Max	15									
Calcium[3]	mg/kg	Max	30									

[1] Source: ISO 8217 Third Edition, Nov. 1, 2005. Petroleum products — Fuels (class F) — Specifications of marine fuels.

[2] A sulfur limit of 1.5% m/m will apply in SO× Emission Control Areas designated by the International Maritime Organization, when its relevant protocol comes into force. There may be local variations.

[3] The fuel shall be free of ULO. A fuel is considered to be free of ULO if one or more of the elements are below the limits. All three elements shall exceed the limits before being deemed to contain ULO.

While the specifications of marine residual fuels listed in Table 10-1 may appear stringent, they actually provide refiners with considerable latitude in the manufacturing of on-specification heavy fuel oils. Because no two refineries operate identically, and because HFO blending depends upon the current operating and economic considerations at a given refinery at a given time, the specific nature of HFOs produced within a single refinery, and certainly between refineries, is expected to be highly variable, while still meeting product specifications. While this may cause some consternation for manufacturers of HFOs, it is precisely this variability that oil spill investigators can use to their advantage in identifying and tracking fugitive marine residual fuels that have been spilled on water.

10.1.3 Marine Fuel Nomenclature and Classification

A complication in the discussion of marine bunker fuels is the naming convention used for the products. Both common and standardized nomenclature systems are regularly used to describe the different grades of marine fuels. Common usage of the catch-all term "bunker fuel" has been used for decades. Traditionally, three types of bunker fuels — A, B, and C — were used to describe these fuels. Bunker A was generally synonymous with No. 2 fuel oil, bunker B was generally synonymous with No. 4 or No. 5 fuel oils, and bunker C, the most commonly used bunker fuel, was generally synonymous with No. 6 fuel oil.

As the demand for marine fuels grew more diverse and intensive in the latter part of the 20th century, various national and international organizations such as the American Society for Testing and Materials (ASTM), the British Standards Institute (BS), and the International Organization for Standardization (ISO) recognized the need to classify and develop standardized specifications for marine fuels (Newbery, 2003; Thomas, 1981). Although a number of standardized marine fuel classification systems were developed, the most widely acknowledged is the structure developed by the ISO. The first ISO specifications for marine fuels were released in 1987, and revised in 1996, at which time the specifications included 19 grades of marine fuel (ISO, 1996). In 2005, the ISO released revised specifications for marine fuels, that now recognizes 14 grades of marine fuels, including 4 distillate and 10 residual grades — the latter of which are inventoried in Table 10-1 (ISO, 2005).

The chemical composition of the four types of distillate marine fuels are not the focus of this chapter. In practice, only two of these are commonly used, namely, marine diesel oil (MDO) and marine gas oil (MGO). MDO is a blend of gas oil and residual oil, and MGO is a high-quality distillate diesel fuel that contains no residual oil blending components.

The principal features that distinguish the 10 grades of residual marine fuel oils are viscosity, pour point, and sulfur, carbon, and metals residue content (Table 10-1); the latter of which is intended to prohibit the use of ULO (as described above). Of the 10 residual grades of marine fuels (Table 10-1), in practice, only five of these are commonly used for marine transportation. These five commonly used fuels occur within two "groups," the names of which are more commonly used within the maritime industry. These two groups are (1) intermediate fuel oil 180 (IFO 180s) and (2) intermediate fuel oil 380 (IFO 380s). These groups' names refer to the maximum permissible viscosities of these fuels at 50°C, 180 and 380 mm^2/s (cSt), respectively (Table 10-1). IFO 180s include ISO grades RME 180 and RMF 180, and IFO 380s include ISO grades RMG 380, RMH 380, and RMK 380 (Table 10-1). Within the IFO 180 and IFO 380 groups, the five individual grades are distinguished by differences in carbon residue, ash, and vanadium content (Table 10-1). Additional nuances have been introduced as recently as 2005 by the ISO to differentiate like-grade bunker fuels with differences in inorganic residuals.

In regard to the behavior of residual fuel oils, it is notable that the current ISO specifications for marine residual fuels includes provisions for two products (RMK 380 and RMK 700; Table 10-1) that closely approach the density of sea water (1030 kg/m^3; Stumm and Morgan, 1996). These very heavy fuels' behavior when spilled poses unique problems for oil spill investigators and responders because of their potential to sink, rather than float, once released into the aquatic environment (Castle et al., 1995; National Academy of Sciences, 1999).

10.2 Forensic Chemistry Considerations

10.2.1 General Chemical Fingerprinting

In the realm of marine heavy fuels, the two most popular groups of heavy fuel oils, IFO 180 and IFO 380, differ largely in their blending formulas. While on average, it is reported that IFO 180 is composed of residual oil blended with about 6% to 7% gas oil-range petroleum, while IFO 380, a more viscous fuel, is composed of residual oil blended with approximately 3% gas oil-range petroleum (Bunker World, 2006), our library of IFO 380 fuels indicates that a much greater percentages gas-oil range hydrocarbons are also possible in heavy fuel oils (see Table 10-2 and discussion that follows). From a forensic chemistry standpoint, it is the combination of the refining and blending processes that impose unique chemical "fingerprints" on IFO 380 HFOs, which oil spill investigators can use to identify and track spilled fuel in the environment.

One of the basic goals in an oil spill fingerprinting investigation is to determine the unique chemical characteristics of the spilled oil, so it may be tracked, linked to a source, and differentiated from other sources, including background petroleum. Collectively, the unique chemical features that describe a particular oil have been termed the products' "fingerprint" (Alimi et al., 2003; Stout et al., 2002; Wang and Fingas, 2003; Morrison, 2000). These "fingerprints" are the basis for qualitative oil spill assessment protocols such as ASTM D-3328, *Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography* (ASTM, 1990); ASTM D-5739, *Standard Practice for Oil Spill Source*

Table 10-2 Weight Percentages of Total Hydrocarbons (THC) and Common Isoalkane Ratios for 71 Worldwide IFO 380 Heavy Fuel Oils

	Min	*Max*	*95th percentile*	*Mean*	*Std Dev*	*% CV**
Gas chromatographable (THC; wt%)	23	100	74	58	13	22
Wt% C_{10}–C_{25}	6	64	49	35	9	26
Wt% C_{25}–C_{45}	6	70	41	23	10	45
Wt% C_{45+}	0	77	57	42	12	30
Isoalkane Ratios						
nC$_{17}$/Pr	0.6	3.0	2.3	1.3	0.5	36
nC$_{18}$/Ph	1.2	2.9	2.1	1.7	0.3	16

*Percent coefficient of variation.

Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry (ASTM, 2000); and quantitative oil spill correlation methods, such as the revised *Nordtest Method for Oil Spill Identification* (Nordtest, 1991; Daling et al., 2002). The challenge for the oil spill investigator is to ascertain what constitutes the most useful chemical features of a "fingerprint" for any given oil.

Oil, once spilled onto water, undergoes a variety of physical and chemical changes due to the forces of environmental weathering (Stout et al., 2002; Rodgers et al., 2000; Fingas, 1988; Atlas, 1981). Evaporation, dissolution, and biodegradation alter or remove many chemical constituents from spilled oil, thereby changing its chemical makeup relative to the original, fresh product (Prince et al., 2003; Durell et al., 1995; Michel and Hayes, 1993; Bobra, 1992; Ostazeski et al., 1995a, 1995b; Shiu et al., 1990; Mackay and McAuliffe, 1988; Anderson et al., 1974; Atlas, 1981; Wang and Fingas, 1994). Because the properties of spilled oil may change in the environment, measures of spilled oils' basic physical characteristics (such as those used to classify the neat fuel; Table 10-1) are virtually meaningless for oil spill identification purposes. More advanced techniques, focused on molecular characterization of oil, have become the methods of choice for oil spill characterization (ASTM, 2000; Stout et al., 2001; Wang and Fingas, 2003; Daling et al., 2002; Nordtest, 1991; ASTM, 1990).

Most sophisticated analytical oil spill identification techniques rely upon gas chromatography (GC) methods. Gas chromatography provides several levels of compositional information. High-quality GC analysis of an oil or environmental sample that contains oil reveals the petroleum residue's overall compositional profile (Stout et al., 2005, 2002; Alimi et al., 2003; Wang and Fingas, 2003). The so-called gas chromatogram is a depiction of the boiling point distribution of the hydrocarbons that compose the oil. The gas chromatogram can allow the investigator to grossly classify the oil (e.g., as crude oil, residual fuel, diesel fuel, etc.). Often, distinctive features such as obvious blending characteristics, or the presence or absence of key hydrocarbon compounds, can be recognized in the gas chromatogram. Next, individual hydrocarbon compounds in the oil can be identified and quantified, usually using gas chromatography with mass spectrometry (GC/MS: Alimi et al., 2003; Stout et al., 2002; Wang and Fingas, 2003). Such compound-specific analyses are focused on measuring chemicals that have been determined to be representative of important components of oil in general and often diagnostic, or source-specific, to a particular oil or fuel blend. The target compounds typically include n-alkanes, acyclic isoprenoids, homo- and heteroatomic 2- through 6-ring parent and alkylated polycyclic aromatic hydrocarbons (PAH, Douglas et al., 1996), and numerous recalcitrant petroleum biomarkers, including hopanes, steranes, and triaromatic steroids (Peters et al., 2005;

Alimi et al., 2003; Stout et al., 2002; Wang and Fingas, 2003; Daling et al., 2002). The applications of biomarker analysis in oil spill assessment are covered thoroughly in Chapter 3 of this book.

Certain of these measured chemicals such as lower-molecular-weight *n*-alkanes, monoaromatics (e.g., BTEX), and lower-molecular-weight PAHs are labile because of weathering. When analyzed, they provide a qualitative assessment of the degree of alteration spilled petroleum has undergone (Stout et al., 2002; Ostazeski et al., 1995a, 1995b; Mackay and McAuliff, 1988; Fingas, 1988; Payne et al., 1987). Other chemicals, such as higher-molecular-weight PAH and biomarkers, are considered to be largely recalcitrant to weathering under most environmental conditions and timescales. These compounds provide diagnostic and reliable information for chemical fingerprinting of spilled oil because the individual compounds or associated compound source ratios remain largely unchanged, even in the face of environmental weathering (Stout et al., 2005, 2002, 2001; Peters et al., 2005; Douglas et al., 1996). Protocols such as those by Nordtest (Nordtest, 1991; Daling et al., 2002) and CEN (see Chapter 7) have been developed to guide the investigator toward use of those diagnostic chemicals most sensitive and reliable in the identification of a particular spilled oil.

10.2.2 Samples and Analytical Methods

In the remainder of this chapter, we will discuss the varied chemical features we have observed among 71 modern residual fuel oils — IFO 380s — in terms of the metrics often used in oil spill fingerprinting investigations. These 71 fuels were obtained directly from marine vessels, or from archived fuels that had been delivered to vessels in ports in the United States, Europe, Asia, and Australia over the past few years. All of the residual fuels studied were "fresh" in that they had not experienced any environmental weathering.

Each of the samples was analyzed for total chromatographable hydrocarbons, *n*-alkanes, and isoprenoid hydrocarbons, 2- through 6-ring PAH compounds, and petroleum biomarkers. The details of these analyses have been described elsewhere (Stout et al., 2002) and are only briefly described herein.

The samples were prepared for analysis by weighing approximately 50 mg of the oil into a tared 10-ml volumetric flask, bringing it to volume in dichloromethane (DCM). A 1-ml aliquot was spiked with surrogate internal standard (SIS; *o*-terphenyl, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{10}) and recovery internal standard (RIS; 5α-androstane, acenaphthene-d_{10}, fluorene-d_{10}, benzo[a]pyrene-d_{12}) and split for quantitative GC/FID and GC/MS analysis as described next.

Gas chromatography-flame ionization detection (GC/FID) analysis was carried out as described by Stout et al. (2001). The target compounds consisted of selected *n*-alkanes and isoprenoids and chromatographic carbon ranges (i.e., C_{10}–C_{25}, C_{25}–C_{45}). Carbon range analysis was performed by employing a standard baseline integration technique. The "window" for each range was determined using the calibration standards. All calibration solution compounds that fell within the window were used to generate the average RF for that range. Areas for SIS and RIS compounds were subtracted. Gas chromatography/mass spectrometry (GC/MS) was conducted using a Hewlett-Packard 6890 Plus GC interfaced to a Hewlett-Packard 5973 mass selective detector (MSD) as described by Stout et al. (2001). Data acquisition was performed in the select ion monitoring (SIM) mode for greatest sensitivity and selectivity. Quantification of target compounds was performed by the method of internal standards using average response factor (RF) of the parent PAH compounds and those of a representative triterpane and sterane from within the 5-point initial calibration.

10.3 General Features of Modern Residual Marine Fuel Oils

Gas chromatographic analysis of petroleum fuels reveals the distinctive boiling point distribution of the chromatographable hydrocarbons that compose the fuels. Common distillates such as diesel or gas oils have predictable and largely similar gas chromatographic fingerprints, by virtue of the fact that they are distilled and blended from a molecular weight-constrained range of hydrocarbons (Speight, 1991; Gary and Handwerk, 1984).

Heavy fuel oils are not compositionally constrained like distillate fuels. Rather, as described earlier, heavy marine fuel oils are blended from residuums, gas oils, and other economically advantageous refinery stocks to achieve basic physical and chemical specifications (Table 10-1; see also Chapter 1 herein). Thus, it is not surprising to find that the gas chromatographic analysis of various residual fuel oils reveals substantial differences in their GC "fingerprints."

Figure 10-1 shows the gas chromatograms for six fresh IFO 380 fuel oils. The specific ISO type (as per Table 10-1) of each of these fuels is unknown to us, but the fuels were all collected from vessels using IFO 380. The variety in the chemical composition expressed in these chromatograms is remarkable and underscores the notion that there is no "typical" residual fuel oil. All six of these example fuels contain the chromatographic features of residuum, for example, a measurable unresolved complex mixture (UCM) of heavy hydrocarbons in the approximately C_{20} to C_{40+} range. However, it is clear from the relative masses of the UCMs in this family of chromatograms that some of the fuels (e.g., Figure 10-1D to F) contain substantially greater amounts of heavier residuum than others (e.g., Figure 10-1A to C). Figure 10-1A shows GC/FID chromatograms for a highly aromatic IFO 380 that is dominated by C_3–C_5 alkyl-benzenes and C_0–C_4 alkyl-naphthalenes within the gas oil range. Figure 10-1B shows the GC/FID chromatogram of another aromatic-rich IFO 380 enriched in C_0–C_4 alkyl-naphthalenes in the gas oil range and a greater proportion of residual range hydrocarbons, including a broad suite of *n*-alkanes. Figure 10-1C shows the GC/FID chromatogram for an IFO 380 predominantly comprised of residual range UCM with resolved compounds including alkyl-naphthalenes, phenanthrenes, and chyrsenes, while little gas oil range material is present. The IFO 380 chromatogram in Figure 10-1D is similar to that of Figure 10-1C but contains a greater proportion of gas oil compounds (e.g., C_3–C_5 alkyl-benzenes and alkyl-naphthalenes) and a greater proportion of unresolved residual range compounds. Figure 10-1E shows the GC/FID chromatograms for an IFO 380 that contains a significant residual range UCM, mostly boiling above C_{25}, the boiling range/viscosity of which is "offset" by a significant gas oil range component dominated by C_3–C_5 alkyl-benzenes and C_0–C_4 alkyl-naphthalenes. Finally, the GC/FID chromatogram in Figure 10-1F shows an IFO 380 dominated by a residual range UCM (with a distinctive profile) and a waxy component, as evidenced by the prominence of C_{30+} *n*-alkanes. Collectively, the GC/FID chromatograms of these IFO 380s demonstrate that they contain varying amounts of a highly aromatic, broad-cut gas oil range (~C_{10}–C_{25}) blending component — as is typical of modern residual fuel production practices (see above and Chapter 1 herein).

The dropoff in several of the UCMs at around C_{40} in Figure 10-1 indicates that these fuels contain a significant mass of high boiling material that is not chromatographable. This mass would include varying amounts of compounds boiling above C_{45}, including resins and asphaltenes, that are not detectable by conventional capillary gas chromatography. The amount of these non-gas chromatographable constituents can, if necessary, be determined by difference (see Figure 10-2) or by liquid chromatography.

Table 10-2 presents the summary statistics for the measurable total hydrocarbons and selected isoprenoid ratios for the 71 worldwide IFO 380 heavy fuel oils. These data were determined from the GC/FID analysis and integrations of individual peak areas and specific carbon ranges. The ratios of *n*-alkanes to isoprenoids (nC_{17}/Pr and nC_{18}/Ph) are commonly used to assess degrees of biodegradation in petroleums. These ratios are shown to

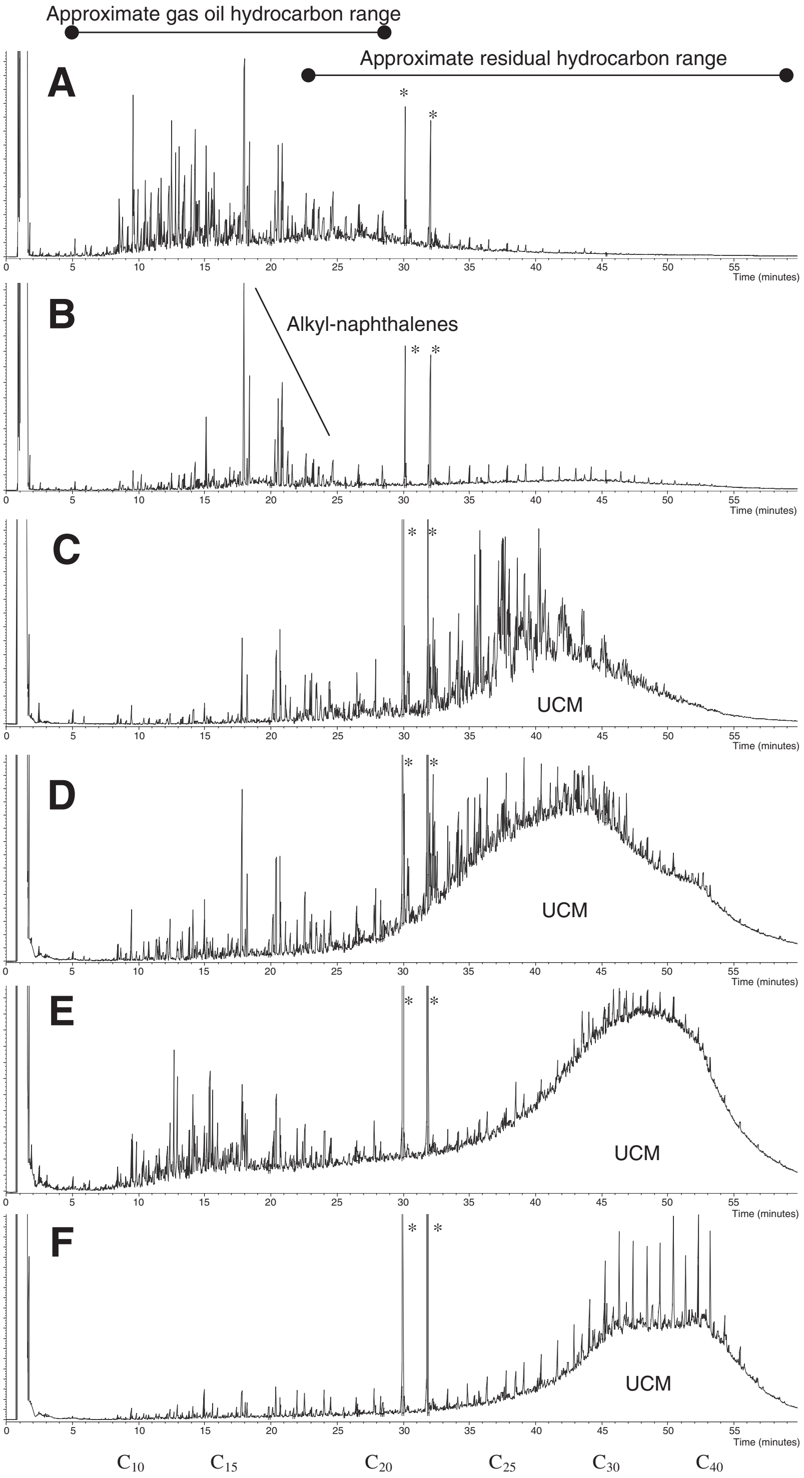

Figure 10-1 Gas chromatographic "fingerprints" of six IFO-380 HFOs, demonstrating the significant variability in chemical compositions in the sample fuel class. * — internal standards.

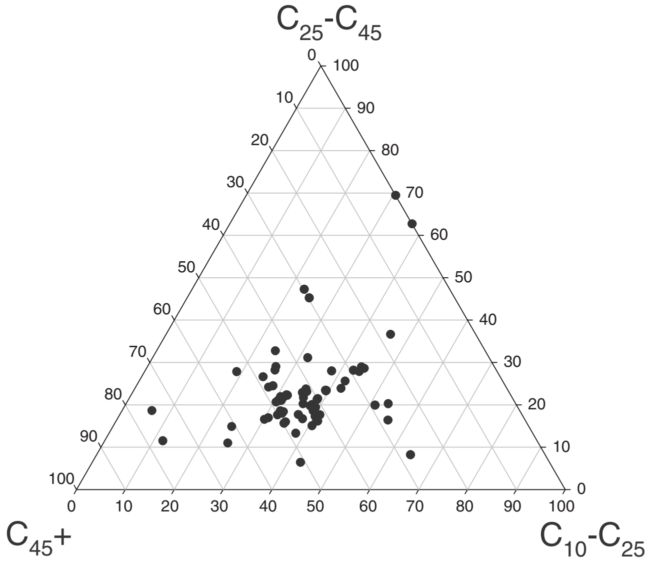

Figure 10-2 Ternary diagram depicting the variability in the bulk hydrocarbon composition among 71 worldwide IFO 380 heavy fuel oil samples. Weight percentages based upon quantitative GC/FID analysis and gravimetric analysis.

vary widely among these "fresh" (unweathered) IFO 380 fuel oils, which indicates that the use of these ratios to assess weathering in a spill investigation needs to consider the spilled oil's starting ratios before describing the degree of weathering among fugitive oils.

The mass of compounds eluting within the gas oil range diluent (C_{10}–C_{25}) versus the residual range residuum (C_{25}–C_{45}) were readily measured by integration of the GC/FID chromatograms. The sum of these two weight percentages provided the total weight percent mass of chromatographable hydrocarbons (THC). The weight percent C_{45+} was then determined by difference (100% minus the weight percent mass of THC, i.e., C_{10} through C_{45}). The statistical results for weight percentages in the 71 IFO 380 fuels studied are given in Table 10-2. These data clearly show what is evident in Figure 10-1, namely, that the proportions of gas oil (or light) diluent (C_{10}–C_{25}), residual range residuum (C_{25}–C_{45}), and nonchromatographable compounds (C_{45+}) vary widely among the IFO 380 fuels studied. The variability in the carbon mass range composition among the 71 worldwide IFO 380 heavy fuel oil samples can be seen in Figure 10-2. Here, the diversity in the carbon-range composition of the samples is clearly evident. The quantitative measurements presented in Table 10-2 and shown in Figure 10-2 parallel the observations noted in the more qualitative gas chromatographic fingerprints shown in Figure 10-1. Inspection of Table 10-2 and Figure 10-2 reveals that two IFO 380 fuels contain very high (>75 wt%) mass percentages of chromatographable hydrocarbons (C_{45+}; Figure 10-2; Table 10-2). Such a high percent mass of C_{45+} compounds indicates that these fuels likely include a high proportion of asphaltenes or nonvolatile inorganic matter. On the other hand, two of the 71 IFO 380 fuels contained 100 weight percent of gas chromatographable material (Figure 10-2). Residual fuels containing no measurable non-chromatographable material clearly are blended using relatively high-quality petroleum stocks, and *de minimis* heavy residuum and <C_{45+} range compounds. This demonstrates that some fuels sold as IFO 380 fuels may actually be higher-quality fuels that are sold (due to local market pressure) as lower-quality IFO 380 fuels. The survey of 71 fuels, however, revealed that both extremes that are evident in Table 10-2 (i.e., excess of 75 wt% nonchromatographable or 0 wt% nonchromatographable mass), would seem atypical for most IFO 380 fuels. On average, IFO 380s studied contained 35 wt% gas oil range, 23 wt% residual range, and 42 wt% nonchromatographable range material (Table 10-2).

10.4 Molecular Variability among Modern Residual Fuel Oils

The variability in the bulk chromatographic features of the 71 IFO 380 heavy fuel oils discussed in Section 10.3 leads to the hypothesis that that there should be significant variability at the molecular level among disparate HFOs. In this section, characteristics of the petroleum biomarkers and polycyclic aromatic hydrocarbons (PAH) in the fuels are discussed, since these compounds often provide the chemical fingerprinting metrics most useful in oil spill investigations — and, in the case of PAH, studies of oil toxicity.

10.4.1 Petroleum Biomarkers

The concentrations and distributions of petroleum biomarkers were analyzed in most of the 71 IFO 380s studied and, also as expected, exhibited widely varying distributions. This variability reflects the inherent "primary" (genetic) variability among crude oil feedstocks and any "secondary" variability imparted during the refining process, for example, blending with cracked intermediate products (see Chapter 1 herein).

The absolute concentration of 17α(H), 21β(H)-hopane was measured in the 71 IFO 380s studied and was shown to vary from 28 mg/kg to 478 mg/kg (median: 134 mg/kg; average: 143 mg/kg; st. dev: 57 mg/kg). This range in concentration is likely the result of different degrees of blending of hopane-bearing residuum and (mostly) hopane-free gas oil range materials. A specific example of the biomarker distribution variability is shown in Figure 10-3. This diagram shows the relative abundances of C_{27}, C_{28}, and C_{29} 14β(H),17β(H) regular steranes measured from the *m/z* 218 mass chromatograms. The HFOs studied exhibit variation in the proportion of C_{29} steranes, a feature that likely reflects the "primary" characteristic related to the abundance of terrestrial organic matter in the parent crude oil feedstock's source rock (Moldowan et al., 1985). Alternatively, it is possible that the increase in C_{29} steranes in some IFO 380s results from an increase in their abundance brought about by distillation, resulting in a residuum enriched in the higher boiling C_{29} steranes — as was observed by Peters et al. (1992). Regardless, the variability among these fuel oils demonstrates the potential utility of biomarkers in distinguishing different residual fuel oils in oil spill investigations (e.g., Stout et al., 2001).

The issue of refining effects on biomarker distributions is reviewed in Chapter 1 herein. Briefly, studies on the effects of crude oil refining on biomarkers have shown that in addition to distillation effects, the thermal stresses experienced during refining, particularly vacuum distillation, can alter various biomarker-based thermal parameters (Peters et al., 1992, Pieri et al., 1996). In one study (Peters et al., 1992), a parent crude oil's biomarkers, with comparable boiling points, were variously depleted or enriched compared to daughter refinery streams (e.g., vacuum gas oil or vacuum residuum). Such changes were attributed to either (1) a preferential preservation (i.e., a greater thermal stability) of certain biomarkers or (2) preferential formation (cracking from bound precursors in the oil) of certain biomarkers during heating. For example, in that study the ratio of C_{29} sterane isomerization (14α(H),17α(H) 20S/(20S + 20R) and $T_s/(T_s + T_m)$ were lower in the vacuum residuum than was observed in the crude oil feedstock, possibly due to the release of the less mature 20R and T_m epimers from high boiling precursors (e.g., asphaltenes) during vacuum distillation.

We evaluated some common thermally driven biomarker parameters for the 71 IFO 380 fuels studied. Cross-plots of two triterpane- and two sterane-based maturity ratios are shown in Figure 10-4. These data show that the C_{31} hopane isomerization ratio (22S/22S + 22R) in all of the HFOs are near equilibrium (~0.55) values found in crude oils (Peters et al., 2005), indicating that the refining

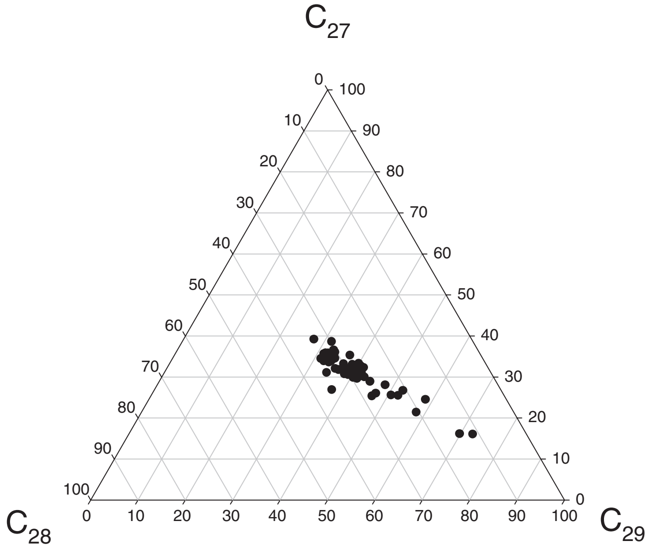

Figure 10-3 Ternary diagrams showing the distribution of C_{27}, C_{28}, and C_{29} regular steranes (5α, 14β, 17β(H) 20S+20R) calculated from absolute concentrations determined from the *m/z* 218 mass chromatogram for 71 IFO 380 residual fuel oils.

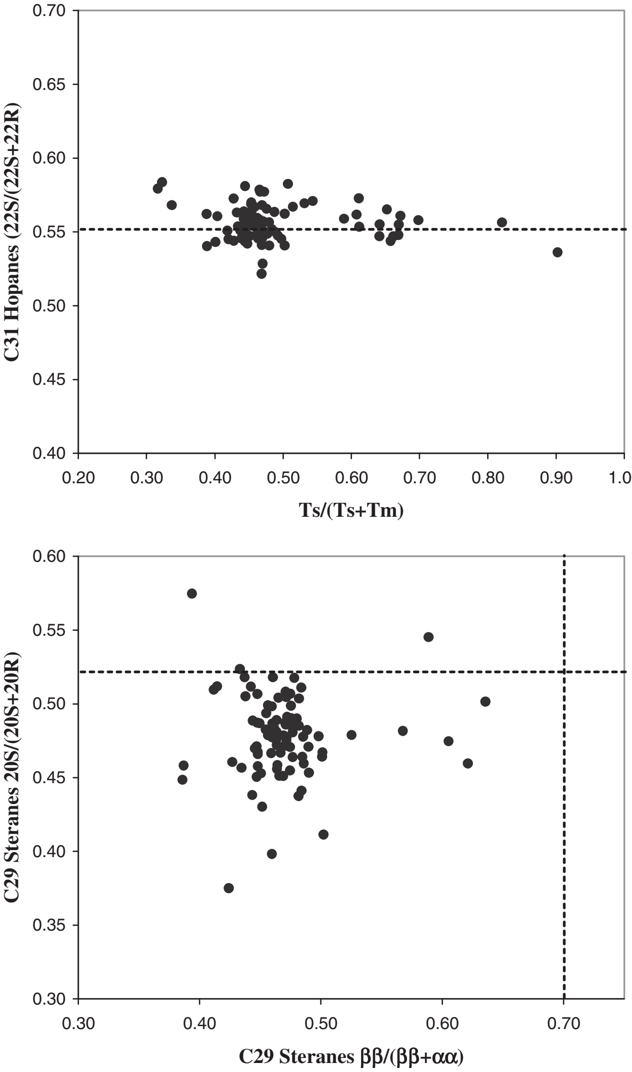

Figure 10-4 Cross-plots of (A) triterpane-based and (B) sterane-based thermal maturity parameters for 71 IFO 380 fuels. Dashed lines show typical maximum (equilibrium) values for crude oils (from Peters et al., 2005). Triterpane ratios both measured on the *m/z* 191 mass chromatograms. 14α(H),17α(H) C_{29} steranes measured on the *m/z* 217 mass chromatogram and 14β(H),17β(H) C_{29} steranes measured on the *m/z* 218 mass chromatogram.

process has not obviously affected this ratio. Similarly, any effect of refining on the other three biomarker ratios plotted is not obvious since most HFOs exhibit values within the ranges anticipated for crude oils. However, two HFOs exhibit a C_{29} sterane isomerization ratio (20S/20S + 20R) above the equilibrium (~0.57) values found in crude oils (Peters et al., 2005). The elevated 20S/(20S + 20R) ratios in these HFOs are likely due to distillation and/or heating effects during the refining process. Regardless, the heterogeneity in the thermal maturity ratios among the 71 IFO 380 fuels studied demonstrates that these (and other) biomarker ratios have value in chemical fingerprinting studies involving HFOs. Biomarker variability among the 71 fuels studied is not discussed further herein, but the reader is directed to Chapter 3 for more information on biomarkers.

10.4.2 Polycyclic Aromatic Hydrocarbons

Homo- and heteroatomic PAH compounds are important chemicals for the characterization and identification of petroleum in the environment, including spilled HFOs. The concentrations and distributions of these PAHs reflect the composition of the original crude oil feedstock from which the residuum is derived, alteration to the petroleum intermediates or residuum that occurs during refinery conversion processes (e.g., cracking, reforming, etc.), and blending of PAHs contained in any viscosity-lowering blending agents (e.g., cracked gas oil and other cutter stocks) into the final fuel mixes.

Table 10-3 presents the summary statistics for the concentrations of PAH and related compounds measured in the 71 worldwide IFO 380 heavy fuel oils studied. Figure 10-5 depicts the mean ±1 standard deviation for the concentrations of individual PAH measured in all of these samples. Significant variations in the PAH concentration among the fuels is evident from this compilation. Most of the PAH compounds are found at concentrations spanning more than an order of magnitude (Table 10-3). Not surprisingly, the PAH distributions in the fresh fuels are, on average, dominated by lower-molecular-weight 2- and 3-ring PAHs such as the naphthalenes and phenanthrenes. (This was evident in several GC/FID chromatograms shown in Figure 10-1.) On average, the IFO 380s exhibit a decreasing abundance of PAH with increasing molecular weight. Each homologous series of alkylated PAH exhibits the anticipated "bell-shaped" profile that is characteristic of petrogenic materials. There are only very low concentrations of 5- and 6-ring PAHs, although these were detected in most samples (Table 10-3).

The prominence of alkyl-naphthalenes in most of the IFO 380 fuels arises largely from the common practice of blending lighter gas oil or other cutter stocks with distillation residuum to control the HFO's viscosity (see Section 10.1.2). In fact, for the majority of samples (~75%), the PAH content of the fuels is comprised of 60–80% C_0–C_4 alkyl-naphthalene, regardless of the total PAH content of the fuel (Figure 10-6). A significant number of the samples, however, diverge from this trend. As illustrated in Figure 10-6, approximately 25% of the samples contain less than 60% total naphthalenes, indicating these fuels were blended with less of a gas oil-range component — or with higher boiling gas oils or cutter stocks whose aromatic content contains proportionally greater amounts of higher molecular weight (3 or more rings) PAH.

The chemical impressions of the PAHs arising from a cracked gas oil cutter stock can easily be seen in the gas chromatographic analysis of blended HFOs (Figure 10-1) and in the PAH distributions. Figure 10-7 shows the PAH histograms for a low- (Figure 10-7A) and high-aromatic (Figure 10-7B) HFO. The relatively higher concentrations of N_0 to N_4 naphthalenes in the high-aromatic HFO is the direct result of blending residuum with an alkyl-naphthalene-rich cracked gas oil (Figure 10-7C). (This cracked gas oil was generated from the coking process at a refinery operating a petroleum coker.) The chemical impressions of the N_0 to N_4 alkyl-naphthalenes are readily

Table 10-3 Homo- and Heteroatomic PAH Composition for 71 Worldwide IFO 380 Heavy Fuel Oils (Concentrations in µg/kg)

	Abvr	*Min*	*Max*	*95th percentile*	*Mean*	*Std Dev*	*% CV*
Naphthalene	N0	108	9,502	3,263	2,129	1,255	59%
C1-Naphthalenes	N1	635	11,296	8,295	5,334	2,210	41%
C2-Naphthalenes	N2	671	10,839	10,085	5,881	2,220	38%
C3-Naphthalenes	N3	504	6,309	5,265	2,927	1,168	40%
C4-Naphthalenes	N4	291	2,823	2,215	1,141	533	47%
Biphenyl	Bph	19	1,731	481	295	215	73%
Acenaphthylene	Acl	ND	ND	NA	ND	ND	NA
Acenaphthene	Ace	20	1,334	325	195	154	79%
Dibenzofuran	DbF	7	215	161	85	40	47%
Fluorene	F0	31	665	311	150	92	61%
C1-Fluorenes	F1	77	767	560	270	145	54%
C2-Fluorenes	F2	146	1,252	874	441	222	50%
C3-Fluorenes	F3	182	1,442	789	438	228	52%
Anthracene	AN	9	120	89	47	21	46%
Phenanthrene	P0	7	1,025	735	358	196	55%
C1-Phenanthrenes/Anthracenes	P1	305	3,515	1,874	1,022	586	57%
C2-Phenanthrenes/Anthracenes	P2	504	5,718	2,542	1,329	831	62%
C3-Phenanthrenes/Anthracenes	P3	398	4,401	2,065	1,013	644	64%
C4-Phenanthrenes/Anthracenes	P4	169	1,870	872	451	265	59%
Dibenzothiophene	D0	19	324	190	83	55	66%
C1-Dibenzothiophenes	D1	86	1,049	536	250	153	61%
C2-Dibenzothiophenes	D2	144	2,002	877	374	275	73%
C3-Dibenzothiophenes	D3	196	1,654	795	348	231	66%
C4-Dibenzothiophenes	D4	104	744	408	190	118	62%
Fluoranthene	FL	5	65.5	40	20	10	50%
Pyrene	PY	25	469	243	125	75	60%
C1-Fluoranthenes/Pyrenes	FP1	100	1,807	630	350	257	73%
C2-Fluoranthenes/Pyrenes	FP2	174	2,718	780	481	370	77%
C3-Fluoranthenes/Pyrenes	FP3	101	2,187	639	373	280	75%
Benz[a]anthracene	BaA	8	275	91	47	33	69%
Chrysene	C0	20	479	156	84	56	67%
C1-Chrysenes	C1	69	1,820	557	303	218	72%
C2-Chrysenes	C2	94	1,893	732	344	242	70%
C3-Chrysenes	C3	27	692	287	126	93	73%
C4-Chrysenes	C4	9	231	137	43	37	87%
Benzo[b]fluoranthene	BbF	3	68.1	23	14	8	59%
Benzo[j/k]fluoranthene	BjkF	2	27.7	15	7	4	60%
Benzo[a]fluoranthene	BaF	ND	ND	NA	ND	ND	NA
Benzo[e]pyrene	BeP	9	159	60	31	20	63%
Benzo[a]pyrene	BaP	4	159	76	30	22	71%
Perylene	Per	2	83.8	52	20	14	69%
Indeno[1,2,3-c,d]pyrene	IND	1	15.1	7	3	3	100%
Dibenz[a,h]anthracene	DBA	1	23.3	15	6	4	66%
Benzo[g,h,i]perylene	Bghi	2	48.9	35	13	9	70%

apparent in the gas chromatographic “fingerprint” of the blended HFO (Figure 10-7D).

From a forensic chemistry standpoint, it is noteworthy that the IFO 380 HFOs contain measurable concentrations of 4-, 5-, and 6-ring PAHs such as fluoranthene, pyrene, the benzofluoranthenes, benzopyrenes, indeno(1,2,3-c,d) pyrene, dibenz(a,h)anthracene, and benzo (g,h,i)perylene (Table 10-3 and Figure 10-5 inset). These chemicals are usually not

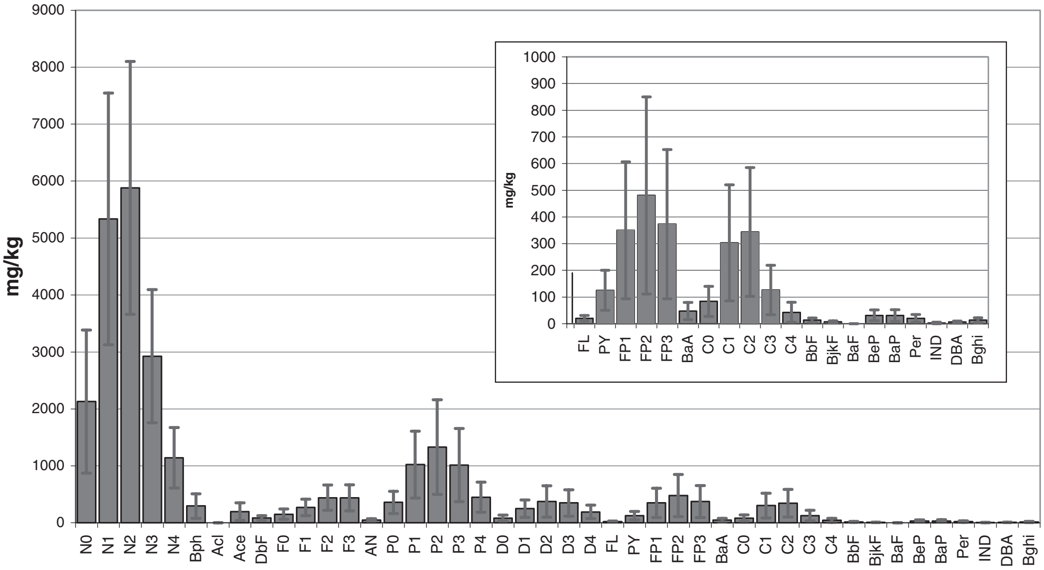

Figure 10-5 Average (±1 standard deviation) concentration of select PAH compounds in 71 worldwide IFO 380 HFOs. See Table 10-3 for compound abbreviations. Inset shows expanded view of 4- to 6-ring PAH.

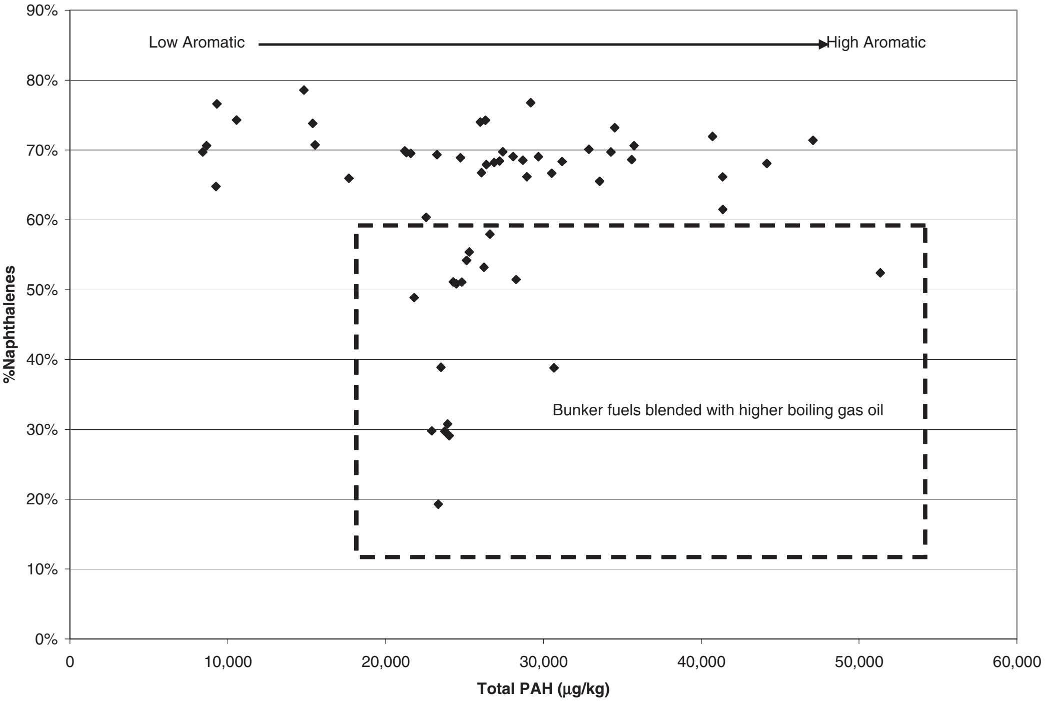

Figure 10-6 Percentage C_0–C_4 naphthalenes of the total PAH in 71 worldwide IFO 380 samples. Total PAH represents sum of 54 analytes from Table 10-3.

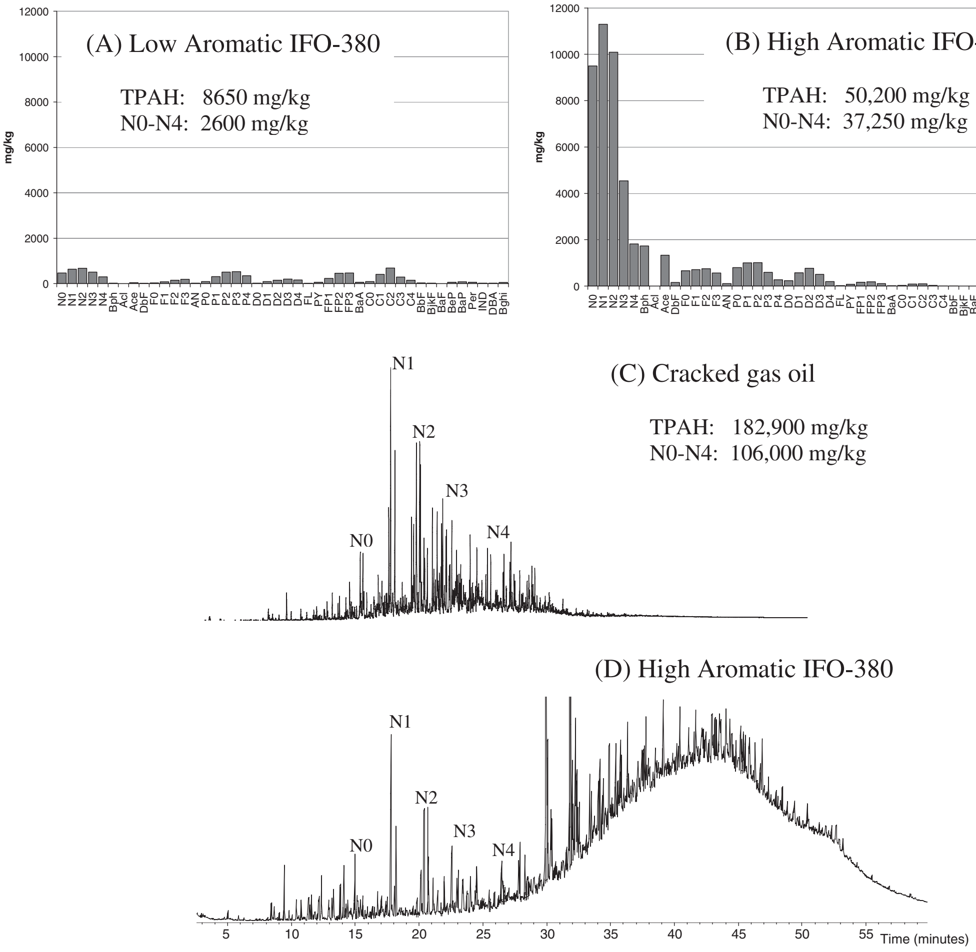

Figure 10-7 Histograms comparing distribution and concentration of PAH in (A) low aromatic IFO-380 and (B) high aromatic IFO-380. Gas chromatogram for (C) high aromatic, cracked gas oil blending stock, and (D) a high aromatic IFO-380 containing a prominent cracked gas oil blending stock.

detectable in most crude oils and distillate fuels because they either are not present or only exist at very low concentrations in such petroleum. These compounds are found in HFOs either because they have become concentrated within the distilled residuum or because they are produced during the distillation of the residuum and/or production of any cracked gas oil cutter stock. Regardless of their genesis, these 4-, 5-, and 6-ring PAH compounds are among the most environmentally stable of the PAHs, and their relative ratios are potentially useful for source identification (Emsbo-Mattingly et al., 2006; Uhler and Emsbo-Mattingly, 2006).

Oil spill investigators have utilized a variety of PAH-based indices and diagnostic ratios to characterize spilled oil in the environment (Stout et al., 2005, 2001; Wang and Fingas, 2003; Burns et al., 1997; Douglas et al., 1996; Henry et al., 1997; Page et al., 1995; ASTM, 1990). Table 10-4 contains a number of potentially diagnostic PAH parameters computed for the 71 worldwide IFO 380 fuel oils studied that provide additional insight into the compositional diversity among the samples. Bulk PAH compositional parameters presented in Table 10-4 offer additional evidence that the aromaticity among IFO 380 fuel oils varies dramatically. Interestingly, not only is there

Table 10-4 Summary Statistics for Certain PAH Diagnostic Metrics for 71 Worldwide IFO 380 Heavy Fuel Oils (See Table 10-3 for Compound Abbreviations.)

	Min	*Max*	*95th percentile*	*Mean*	*Std Dev*	*% CV*
PAH Metrics						
Total PAH (mg/kg, oil)[1]	8,414	51,345	42,757	27,171	8,974	33%
Priority Pollutant PAH (mg/kg, oil)[2]	616	12,575	4,768	3,227	1,539	48%
%TPAH as PP PAH	5.84	25.1	13.9	11.7	2.7	24%
Total Naphthalenes (mg/kg, oil)	0.26	3.73	2.90	1.74	0.67	39%
Total Dibenzothiophenes	0.06	0.58	0.28	0.12	0.08	65%
LPAH (mg/kg, oil)	5,465	49,289	39,480	24,751	8,591	35%
HPAH (mg/kg, oil)	791	13,148	4,076	2,419	1,666	69%
%LPAH	63.1	98.2	96.2	90.2	6.8	7%
%HPAH	1.77	36.9	25.4	9.8	6.8	69%
Selected Diagnostic Ratios						
MPI[3]	1.46	3.43	2.7	2.5	0.22	9%
MPR[3]	3.27	5.05	4.8	4.4	0.30	7%
%2MA/P1	4.21	8.86	8.1	6.9	0.97	14%
D2/P2	0.06	0.77	0.5	0.3	0.12	41%
D3/P3	0.08	0.86	0.7	0.4	0.15	40%
FL/PY	0.11	0.25	0.2	0.2	0.02	13%
BaA/CO	0.22	0.65	0.6	0.6	0.07	12%
AN/P0	0.06	0.18	0.2	0.1	0.02	18%

[1] Σ54 PAH and alkylated PAH per Table 3.

[2] Σ16 US EPA Priority Pollutant PAH.

[3] Methylphenanthrene index and ratio, respectively. See Radke et al. (1982).

[4] % 2-methyl-anthracene/Σmethyl-phenanthrene isomers.

significant spread in the total PAH content among HFOs (largely indicative of the proportions of high-aromatic, cracked gas oil blending stock used in the formulation of the fuel) but there is significant variation in the percentage of low-molecular-weight PAH (LPAH; i.e., sum of 2- through 3-ring PAHs) versus high-molecular-weight PAH (HPAH; i.e., sum of 4- through 6-ring PAHs). This almost certainly is consistent with the concept that the distribution of PAHs in HFOs is largely a function of the type and boiling range of cutter stock used to blend IFO 380 and the concentrations and types of PAHs that exist in the base residuum.

Inspection of Table 10-4 reveals that there are wide variations in the sulfur-containing dibenzothiophene concentrations among the samples that likely reflect the total sulfur content of the crude oil feedstocks used in the production of the residuum and cutter stocks (Song, 2000). Ratios of the C_2- and C_3-dibenzothiophenes relative to the respective C_2- and C_3-phenanthrenes are commonly used source ratios in oil spill studies (Stout et al., 2005, 2001; Burns et al., 1997; Douglas et al., 1996; Page et al., 1995). A plot of the source-specific D2/P2 versus D3/P3 ratios shows a wide spread in values among the 71 IFO 380 fuels studied, suggesting that these (and other) ratios hold the potential for differentiation and correlation among HFOs in oil spill studies (Figure 10-8). Notably, higher D2/P2 and D3/P3 values up to 1.6 and 2.2, respectively, have been observed in a high-sulfur residual fuel that was not among the 71 studied herein (Douglas, unpublished). It is interesting to note that the spread in the dibenzothiophene ratios among the 71 worldwide heavy fuel oils studied is not a strong function of total PAH concentration (Figure 10-8B). This is a favorable finding from a chemical fingerprinting standpoint, because it means that the diagnostic C2- and C3-dibenzothiophene to phenanthrene ratios are useful diagnostics for both lower aromatic and higher aromatic HFOs.

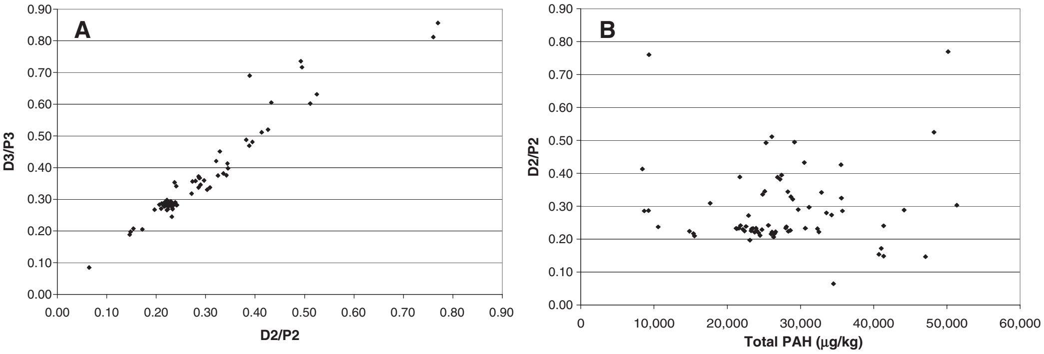

Figure 10-8 Cross-plots of (A) the range in of the diagnostic source ratios D2/P2 and D3/P3 and (B) the relationship between D2/P2 and total PAH in 71 worldwide IFO 380 heavy fuel oil samples.

10.5 Distinguishing Heavy Fuel Oils from Crude Oil

Many heavy fuel oils are readily recognized as manufactured products by the characteristic chromatographic (e.g., distillation) and molecular chemical features (e.g., presence of cracked petroleum products), some of which have been illustrated earlier in this chapter. For example, the clear presence of mixtures of residuum and broad (or narrow) boiling gas oil range cutter stocks, or the obvious presence of significant amounts of aromatic compounds such as alkyl-benzenes, alkyl-naphthalenes, and alkyl-phenanthrenes that arise from blending with high-aromatic, cracked gas oils (e.g., Figure 10-7C). However, among the diverse types of HFOs is a small subset that, at first inspection, shares many chromatographic and chemical similarities with evaporated or otherwise slightly weathered crude oil. Debate among oil spill fingerprinting experts can arise in instances where spilled oil — be it HFO or weathered crude oil — can be confounded by the possible presence of the other.

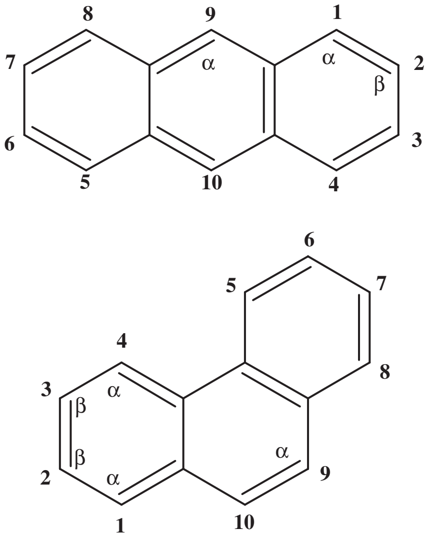

Figure 10-9 Structures of (A) linear 3-ring anthracene molecule and (B) nonlinear 3-ring phenanthrene molecule.

In cases where basic gas chromatographic analysis of a spilled oil residue is equivocal about the nature of the petroleum (i.e., weathered crude oil or manufactured HFO), we have relied upon in-depth analysis of PAH isomers and other compounds such as petroleum biomarkers, in an effort to identify subtle chemical markers that may serve to distinguish weathered crude oil from manufactured heavy fuel oil. A useful approach in such instances is careful inspection of PAH isomers whose presence is most likely due to refining — in particular, thermal and catalytic cracking. Consider the distribution of 3-ring methyl-PAHs (i.e., linear methyl-anthracenes and nonlinear methyl-phenanthrenes) (Figure 10-9). There are three possible isomers of methyl-anthracene and five isomers of methyl-phenan-

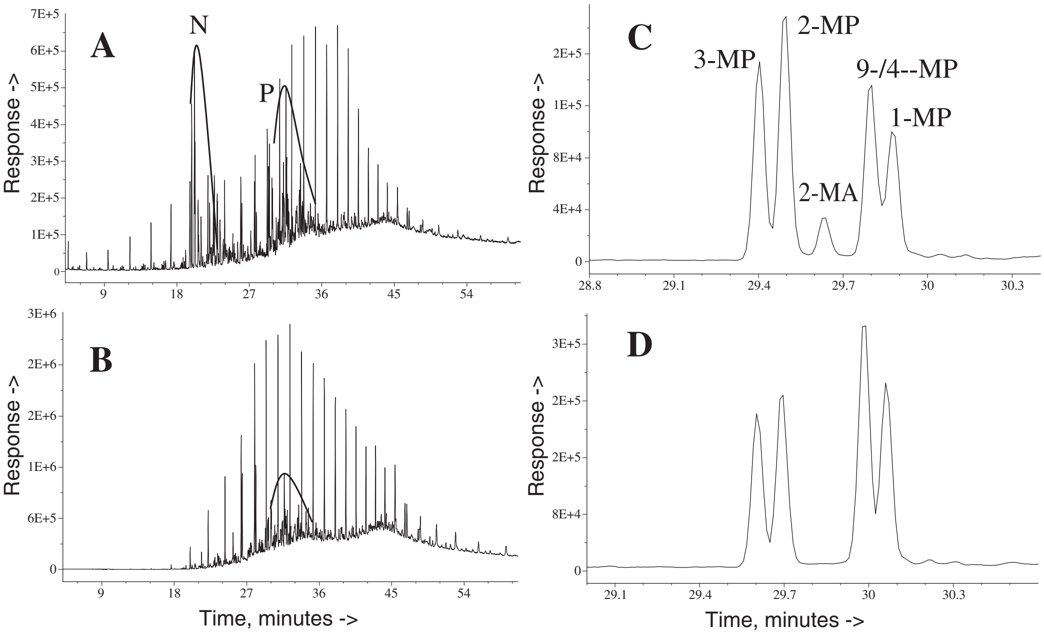

Figure 10-10 GC/FID chromatograms for (A) an unweathered IFO 380 fuel and (B) moderately evaporated crude oil and partial *m/z* 192 mass chromatograms for (C) the unweathered IFO 380 shown in (A) and (D) the moderately evaporated crude oil shown in (B). N — alkyl-naphthalenes, P — alkyl-phenanthrenes; MP — methylphenanthrene, MA — methylanthracene.

threnes that can be seen in gas chromatography/mass spectrometry *m/z* 192 mass chromatograms.

The proportions of the five methyl-phenanthrene isomers (which appear as four prominent peaks in the *m/z* 192 mass chromatogram of most oils; see Figure 10-10) have been used extensively to monitor the thermal stresses imposed under geologic heating of coals and oils, with the 3- and 2-methylphenanthrene (β-type) isomers proving more stable than the 9-, 4-, and 1-methylphenanthrene (α-type) isomers (e.g., Radke et al., 1982, 1990). These studies have shown that although methyl-anthracenes are present in low-rank coal extracts, they quickly are decreased (relative to methyl-phenanthrenes) or lost in the extracts of higher-rank coals (Radke et al., 1982). As such, it is reasonable that the linear methyl-anthracenes are considerably less thermodynamically stable than the nonlinear methyl-phenanthrenes. Therefore, methyl-anthracenes generally are absent or present in only low concentrations (relative to phenanthrenes) in most crude oils, which are produced slowly over long periods of time under geologic heating conditions. On the other hand, methyl-anthracenes, particularly 2-methyl-anthrancene (the only β-type isomer), are prominent components in pyrolytic organic materials that are produced under rapid heating conditions (e.g., coal tar). By analogy, 2-methyl-anthracene may be produced under some pyrolytic conditions experienced in the course of refining (e.g., thermal cracking).

2-Methyl-anthracene is easily resolved in the *m/z* 192 mass chromatograms for most polar GC capillary columns (Figure 10-10). As such, the presence of 2-methyl-anthracene (in conjunction with other particular aromatic compounds) might serve as an indicator of the presence of a cracked gas oil blending stock in the HFO — and thereby allow distinction from crude oil. In the 71 IFO 380 fuels studied herein, 2-methyl-anthracene was detected in all of them and comprised between 4.2%

and 8.9% of the total C2-phenanthrenes/anthracenes measured on the *m/z* 192 mass chromatogram (Table 10-4).

An example of this potential is shown in Figure 10-10. The GC/FID chromatograms for an unweathered IFO 380 and a moderately evaporated crude oil are shown in Figure 10-10A and 10-10B, respectively. These two oils share many common features, which is not surprising since the IFO 380 was produced from the same type of crude oil feedstock as is depicted in Figure 10-10B. Qualitative comparison between these would reveal a relative prominence of alkyl-naphthalenes and alkyl-phenanthrenes in the IFO 380 (relative to the *n*-alkanes), which are much lower in abundance in the crude oil. This difference is attributable to the presence of a cracked gas oil component in the IFO 380 — which, of course, is absent in the crude oil. Inspection of the corresponding *m/z* 192 mass chromatograms (Figure 10-10C and D) reveals a distinct difference in the distribution of methyl-phenanthrene isomers and in the prominence of 2-methyl-anthracene. The IFO 380 fuel oil contains a greater proportion of 2- and 3-methyl-phenanthrene (i.e., the more thermally stable β-type isomers) and 2-methyl-anthracene than the crude oil. This difference would also be consistent with the presence of a cracked gas oil component in the IFO 380, in which thermal stability of the 2- and 3-methyl-phenanthrene (β-type) isomers and the formation of 2-methyl-anthracene produce a fingerprint (Figure 10-10C) that is distinct from the crude oil (Figure 10-10D).

In an oil spill scenario in which the IFO 380 shown in Figure 10-10A were to experience evaporative weathering, the presence of the cracked gas oil component in the GC/FID would not be nearly as obvious. Under this circumstance, the weathered IFO 380 might be confused with a weathered crude oil (such as in Figure 10-10B). However, despite weathering, the presence of 2-methlyl-anthracene among the methyl-phenanthrenes would provide evidence that the spilled oil was actually HFO and not crude oil.

As described in Section 10.4.1, biomarker thermal maturity indicators may also provide a means to distinguish HFO from crude oils, where the samples in question otherwise share many chromatographic and chemical similarities. The basis for this is that HFO contains distillation residuums that are subject to alteration under the pressure and temperature conditions, particularly during vacuum distillation, that can alter thermal maturity parameters (Peters et al., 1992). Sometimes this alteration may be beyond reasonable for naturally heated crude oils (e.g., see outliers in Figure 10-4B).

An example of this potential is demonstrated in the biomarker-based thermal maturity ratios shown in Table 10-5. These data were collected from a crude oil and from five asphalt samples made from the vacuum distillation residuums of that crude oil. (Admittedly, petroleum asphalts are not HFOs, but both

Table 10-5 Biomarker-Based Thermal Maturity Parameters Measured in Five Asphalts (S_1–S_5) Manufactured with Vacuum Distillation Residuum Derived from the Parent Crude Oil Source

Thermal Parameters	*Asphalt Samples*					*Parent Crude Oil*	
	S1	*S2*	*S3*	*S4*	*S5*	*Original*	*Duplicate*
$Ts^1/(Ts + Tm^2)$	0.52	0.50	0.48	0.56	0.44	0.29	0.33
$X^3/(X + Ts)$	0.24	0.27	0.29	0.35	0.39	0.00	0.00
C29 Steranes (ββ)/(ββ + αα)	0.49	0.49	0.49	0.51	0.49	0.27	0.26

[1] Ts = 18α(H)-22,29,30-Trisnorneohopane.

[2] Tm = 17α(H)-22,29,30-Trisnorhopane.

[3] X = 17α(H)-Diahopane.

products contain the vacuum distillation residuums of crude oil that has been subjected to extensive heating and pressures.) Each of the thermal parameters in the asphalts is elevated relative to the parent crude oil. The increase in each of these parameters argues for the formation or release of the more thermally stable Ts, 17α(H)-diahopane, or 14β(H), 17β(H) C_{29} steranes during heating. In a spill scenario, the increased values of these parameters might allow for the distinction between a refined product containing vacuum residuums (in this case, asphalt) and crude oil.

10.6 Conclusion

Modern residual marine fuels are economically important fuels used throughout the world in the commercial maritime shipping industry. Once a simpler fuel composed largely of atmospheric residuums, modern (post-1970s) HFOs are mixtures of highly refined, atmospheric and vacuum residuum, blended with thermally and catalytically cracked gas oils or other (typically low-value) refinery intermediate stocks. The complexities and economics of producing modern HFOs have resulted in heavy fuel products of remarkable chemical diversity, which can prove useful in oil spill investigations relying upon chemical fingerprinting.

The compositional variety of 71 modern IFO 380 fuel oils obtained from vessels and ports around the world has been illustrated in this chapter. Often, distinctive gas chromatographic fingerprints of these fuels include a prominence of aromatic-rich gas oil range (C_{10}–C_{25}) components, admixed with a broad-boiling residual range (C_{25}–C_{45}) component consisting mostly of an unresolved complex mixture (UCM) and varying amounts of resolved paraffins and PAHs. As such, the unique gas chromatographic fingerprints of an HFO can potentially be used as a reliable indicator in an oil spill investigation — particularly in the early phase of a spill before significant weathering has occurred. However, the gas chromatographic fingerprint of an HFO will alter due to postspill weathering, thereby ultimately confounding the use of simple qualitative gas chromatographic comparisons in oil spill identification and tracking. Fortunately, the detailed molecular chemistry of HFOs — including petroleum biomarkers and PAHs — have been shown in this chapter to be very diverse, meaning that unique and reliable chemical metrics — source ratios — can be developed for use in sophisticated oil spill tracking and source correlation analyses. The use of appropriate forensic chemistry techniques, coupled with knowledge of the refining chemistry of HFOs and their behavior on water, affords oil spill investigators the best opportunity to confidently identify and track the fate of spilled heavy fuel oils in the environment.

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