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Evaluation of Environmental Samples Containing Heavy Hydrocarbon Components in Environmental Forensic Investigations

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This article presents a procedure to evaluate and characterize environmental samples containing mixtures of hydrocarbons over a wide boiling range of materials that include fuels and other products used in commerce. The range of the method extends to the higher boiling and heavier molecular weight hydrocarbon products in the range of motor oil, bunker fuel, and heavier residue materials. The procedure uses the analytical laboratory technique of high-temperature simulated distillation along with mathematical regression of the analytical data to estimate the relative contribution of individual products in mixtures of hydrocarbons present in environmental samples. An analytical technique to determine hydrocarbon-type distributions by gas chromatography–mass spectrometry with nitric oxide ionization spectrometry evaluation is also presented. This type of analysis allows complex hydrocarbon mixtures to be classified by their chemical composition, or types of hydrocarbons that include paraffins, cycloparaffins, monoaromatics, and polycyclic aromatic hydrocarbons. Characteristic hydrocarbon patterns—for example, in the relative distribution of polycyclic aromatic hydrocarbons—are valuable for determining the potential origin of materials present in environmental samples. These methods provide quantitative data for hydrocarbon components in mixtures as a function of boiling range and "hydrocarbon fingerprints" of the types of materials present. This information is valuable in assessing environmental impacts of hydrocarbons at contaminated sites and establishing the liabilities and cost allocations for responsible parties.

Keywords: hydrocarbon fingerprints, high molecular weight (HMW) hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), petroleum-derived (petrogenic) and combustion-derived (pyrogenic) hydrocarbons, jet fuel, diesel fuel, #6 fuel oil (bunker fuel), motor oil, coal tar pitch, high-temperature simulated distillation (HTSD), gas chromatography–mass spectrometry (GC-MS), nitric oxide ionization spectrometry evaluation (NOISE), mathematical regression, sediments, environmental contaminants, responsible party liabilities, CERCLA (Comprehensive Environmental Response Compensation and Liability Act or "Superfund").

Introduction

The occurrence of hydrocarbon contamination found in the environment often leads to an investigation to assess the nature and extent of contamination and then to a remediation and restoration of the contaminated area. Environmental forensic work commonly includes a contamination site assessment, recommendation of remediation and restoration, and a determination of the allocation of costs among responsible parties to clean up and restore the site. It is essential to know the chemical nature of the contaminants present in order to determine appropriate remediation and restoration. Establishing the source(s) of contamination is important in understanding the occurrence of the contamination and in determining who is responsible for it.

Contaminant source determination depends in part on a knowledge of current and historical operations and usage of the site, and whether present-day contaminants represent the original contaminants or alterations of the original materials. An understanding of potential influences, such as natural weathering and biodegradation processes, on chemical contaminants and their precursors is required, as is an understanding of the nature of the possible transport and migration history of the contaminants. The determination of origin of contamination is often complicated due to multiple industrial usage and source contributions for a given site over time. Some examples of environmental contaminants and their potential sources that can be encountered in environmental forensic investigations include hydrocarbons and metals from urban runoff and municipal outfalls; pesticides from farming; petroleum hydrocarbons, metals, and chemicals in oil and gas production; petroleum hydrocarbons in petroleum refining and pipeline operations; polycyclic aromatic hydrocarbons (PAHs), tars, and metals associated with coal gasification and processing; chemicals in manufacturing; and the handling and storage of transportation fuels and oils.

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This article presents an analytical procedure to characterize environmental samples containing mixtures of hydrocarbons that include heavier molecular weight hydrocarbon products in the boiling range of motor oil, bunker fuel, and higher boiling residue materials. The analytical laboratory techniques of high-temperature simulated distillation (HTSD) and mathematical regression of the analytical data are used to estimate the relative contribution of individual products in mixtures of hydrocarbons present in environmental samples. Also presented is an analytical technique to determine hydrocarbon-type distributions by gas chromatography–mass spectrometry (GC-MS) with nitric oxide ionization spectrometry evaluation (NOISE). This technique is valuable for "fingerprinting" PAHs found in environmental samples to determine the possible origin of hydrocarbons present.

The data from these analytical techniques are valuable in assessing environmental impacts over a selected study area and establishing liabilities and cost allocations for responsible parties at contaminated sites. CERCLA (Comprehensive Environmental Response Compensation and Liability Act or "Superfund") retroactive liability for adverse environmental impacts has resulted in cleanup costs for parties responsible for operations contributing high molecular weight (HMW) hydrocarbon contamination into the environment.

Hydrocarbon Fingerprinting

Hydrocarbon fingerprinting techniques have been reported in a number of environmental analysis and forensic studies (Bruce and Schmidt, 1994; Sauer and Uhler, 1994; Khalili et al., 1995). Petroleum and combustion-derived (e.g., coal tar) hydrocarbons, for example, have distinguishing compositional patterns or "chemical fingerprints" in the relative amounts of the types of PAHs present, which arise primarily from different thermal processes involved in their formation.

The identification of potential sources of hydrocarbons in a sample in terms of commercial fuels or products has been attempted by comparing the distribution "pattern" of components in a sample or noting the concentration of one or more of those components compared to a known standard. In general, these efforts in the past have been limited to a section of the hydrocarbon spectrum from gasoline through motor oil. Higher molecular weight hydrocarbons are not currently identified by EPA-approved analytical methodology such as EPA 8015 (USEPA, 1996). It has not been possible, therefore, to compare samples containing heavier hydrocarbons in the boiling range higher than motor oil with currently accepted environmental methodology.

High-Temperature Simulated Distillation

In recent years the environmental analysis work carried out in our laboratory has effectively made use of the analytical laboratory technique of high-temperature simulated distillation (HTSD) to extend the boiling range characterization of hydrocarbons and other organic materials present in soils and sediments and other matrices associated with environmental contaminated site investigations. This is a gas chromatographic method that is frequently used in the characterization of refinery products. The HTSD method has been described in detail in previous publications (Villalanti et al., 1995, 1997, 2000; Golden et al., 1995; Raia et al., 2000).

The HTSD method is applicable for the analysis of a wide boiling range of materials that extends from the low- and mid-range hydrocarbons in gasoline, diesel, and jet fuel to the higher boiling hydrocarbons in motor oil, bunker fuel, and finally to heavier asphaltic and residue materials. This covers the range from about 97°F (36°C) to 1350°F (732°C), which corresponds to n-paraffins in the carbon number range of about C5 to about C108. HTSD thus allows for a more complete picture of the entire range of light to heavier hydrocarbons from both petroleum- and combustion-derived sources as well as other sources.

Gas Chromatography–Mass Spectrometry with Chemical Ionization

Hydrocarbon-type distributions in samples are determined in our laboratory by gas chromatography–mass spectrometry (GC-MS) with a chemical ionization technique that uses nitric oxide ionization spectrometry evaluation (NOISE). This analysis yields a simplified mass spectra that allows complex hydrocarbon mixtures to be classified by their chemical composition, or types of hydrocarbons. Included are paraffins, cycloparaffins, and aromatics in the boiling range between about 250°F (121°C) and 1000°F (538°C). This method is applicable in the n-paraffin carbon number range that extends up to about C40, and only in recent years has it been available other than within large research organizations. The technique is described in detail in previous publications (Dzidic et al., 1992; Wadsworth and Villalanti, 1992; Villalanti and Wadsworth, 1993).

The NOISE method has been applied in our laboratory for "fingerprinting" PAHs in efforts to determine the possible origin of hydrocarbon contaminants in environmental samples. The use of PAH fingerprinting concepts have been reported in earlier studies (Bruce and Schmidt, 1994; Sauer and Uhler, 1994). PAHs thought to be derived from petroleum (petrogenic) have been characterized by "bell"-shaped patterns of PAH distributions enriched in C2 and/or C3 alkyl PAHs, and in 2- and 3-membered ring PAHs. The PAHs thought to be derived from combustion processes (pyrogenic) have "skewed" pattern distributions and are enriched in parent nonalkylated (C_0) PAHs, and in 4-, 5- and 6-ring PAHs. This difference is explained as the result of higher temperatures of formation of pyrogenic materials compared to petrogenic processes.

Methods

In the oil and gas industry, petroleum producers and refiners have engaged in the characterization of reservoir fluids and refined products for many years. Such characterization is needed for projecting and optimizing the yield of commercial products from the crude oil in a reservoir that enters the refinery for processing.

The laboratory analysis procedure known as simulated distillation is a standard procedure (ASTM Method D2887) used in petroleum refining operations for the characterization of hydrocarbons (ASTM, 1997). This method is very adequate for the intended boiling range of up to 1000°F (538°C) but does not cover heavier hydrocarbon materials. HTSD extends the D2887 method to higher boiling materials and is currently in proposed ASTM status for characterization of the heavier molecular weight hydrocarbons present in the boiling range up to about 1382°F (750°C). The proposed extension of the method is in the interlaboratory analysis stage of development and is expected to be accepted once evaluation of all the results is completed.

Simulated distillation determines the volatility distribution of organic matter in samples as a function of boiling temperature. The results of the analysis of a sample can be shown in terms of the boiling points of normal paraffins for ease of viewing

Table 1. *High-temperature simulated distillation (HTSD) analysis report*

Data File Name: C:\HPCHEM\1\DATA\0628A\005F0801.D

Instrument: 1
Operator: Triton Analyt.
Acquired on: 28 Jun 00 11:52 PM
Processed on: 03 Jul 00 8:49 AM
Sample name: HC-S-19
Method name: MHC30.MTH ISTD
Calc. based on: ESTD
Sequence name: 0628A

Blank used: C:\HPCHEM\1\DATA\0628A\085F0202.D
BP calib. used: C:\HPCHEM\1\DATA\0628A\090F0101.D
Reference used: C:\HPCHEM\1\DATA\0628A\095F0301.D

Recovery(%): 51.8 found, 100% recovery assumed
Resp. factor: 1.254E-10
IBP: 468°F
FBP: 1333°F

Vial: 5
Injection: 1
Seq. line: 8

Sample Amt: 0.0700
Amt: 0.0000
Weight CS2: 1.7277
Cryogenic sequence

Threshold set: 100.0
Start elution: 2.00 Set
End elut. at: 44.84

Analysis results: %Weight versus boiling point

%	BP(°F)	%	BP(°F)	%	BP(°F)	%	BP(°F)
1	514	26	752	51	847	76	993
2	563	27	761	52	853	77	1000
3	581	28	765	53	858	78	1008
4	606	29	766	54	864	79	1017
5	628	30	770	55	869	80	1027
6	630	31	772	56	876	81	1036
7	631	32	775	57	882	82	1045
8	639	33	779	58	885	83	1056
9	640	34	781	59	889	84	1067
10	646	35	783	60	894	85	1078
11	658	36	784	61	898	86	1089
12	666	37	788	62	901	87	1099
13	671	38	793	63	907	88	1112
14	684	39	797	64	914	89	1125
15	693	40	801	65	919	90	1137
16	700	41	806	66	928	91	1150
17	707	42	813	67	934	92	1166
18	711	43	820	68	939	93	1180
19	712	44	826	69	945	94	1197
20	714	45	829	70	950	95	1213
21	718	46	833	71	955	96	1234
22	723	47	837	72	961	97	1260
23	732	48	838	73	970	98	1285
24	738	49	842	74	979	99	1315
25	741	50	844	75	986		

Analysis results: Table of cutpoints

BP(°F)	%	BP(°F)	%	BP(°F)	%	BP(°F)	%
480	0.5	700	16.0	900	61.6	1100	87.1
650	10.4	800	39.8	1000	77.1	1200	94.2

and interpretation. The output of the HTSD as used in this technique is a volatility plot in which the percent weight yield (both incremental and cumulative) of a sample, i.e., the amount of hydrocarbon material boiling in a narrow boiling point range, is plotted at each carbon number corresponding to the normal paraffin of that boiling point.

It is important to recognize that for environmental samples such as soils and sediments, extraction of the sample is typically required for the chromatographic analysis of hydrocarbons present. To determine the lower boiling hydrocarbons (such as those present in gasoline, jet, and diesel), it is important to use a solvent that allows measurement of the lower boiling hydrocarbons in the extract with minimal chromatographic interference from the solvent. Extraction procedures typically follow one similar to EPA Method 3550 (USEPA, 1996). In the studies presented here, methylene chloride was used as extraction solvent both for extraction efficiency and for its relatively low boiling point (104°F or 40°C).

For the higher boiling HMW hydrocarbons it is advantageous to make a gravimetric determination of the total extractable hydrocarbons that can be recovered after solvent removal. A weighed portion of the extractable material from the sample is used in the HTSD analysis. This facillitates sample-to-sample comparisons of sediment/soil samples that contain widely varying concentration levels of extractable hydrocarbons. Again, it is important to use a lower boiling solvent, which, after removal, will allow for recovery and measurement of as much as possible of the lower as well as higher boiling components in the sample. The gravimetric determination of extractables is used to account for both nonextractable material in the original sediment/or soil sample as well as extractable heavier hydrocarbon material that may not be fully eluting and detected in the chromatographic HTSD analysis.

It should be emphasized that the solvent removal step of the gravimetric procedure will preclude the analysis of the extractable lower boiling hydrocarbons such as those in gasoline, jet, and part of diesel. Compounds up to about C15 and some higher carbon components are partially lost in the gravimetric procedure. Those components, however, could be determined in a weighed aliquot of the extract before the gravimetric step is done.

In the chromatographic analysis of the hydrocarbon content of a sample it is normally assumed that the response of the detector (generally a flame ionization detector or FID) to the chromatographable hydrocarbons is the total hydrocarbon content of the sample. For HMW products that contain various types of hydrocarbons this assumption may have error due to response-factor differences of the detector and to the fact that some very

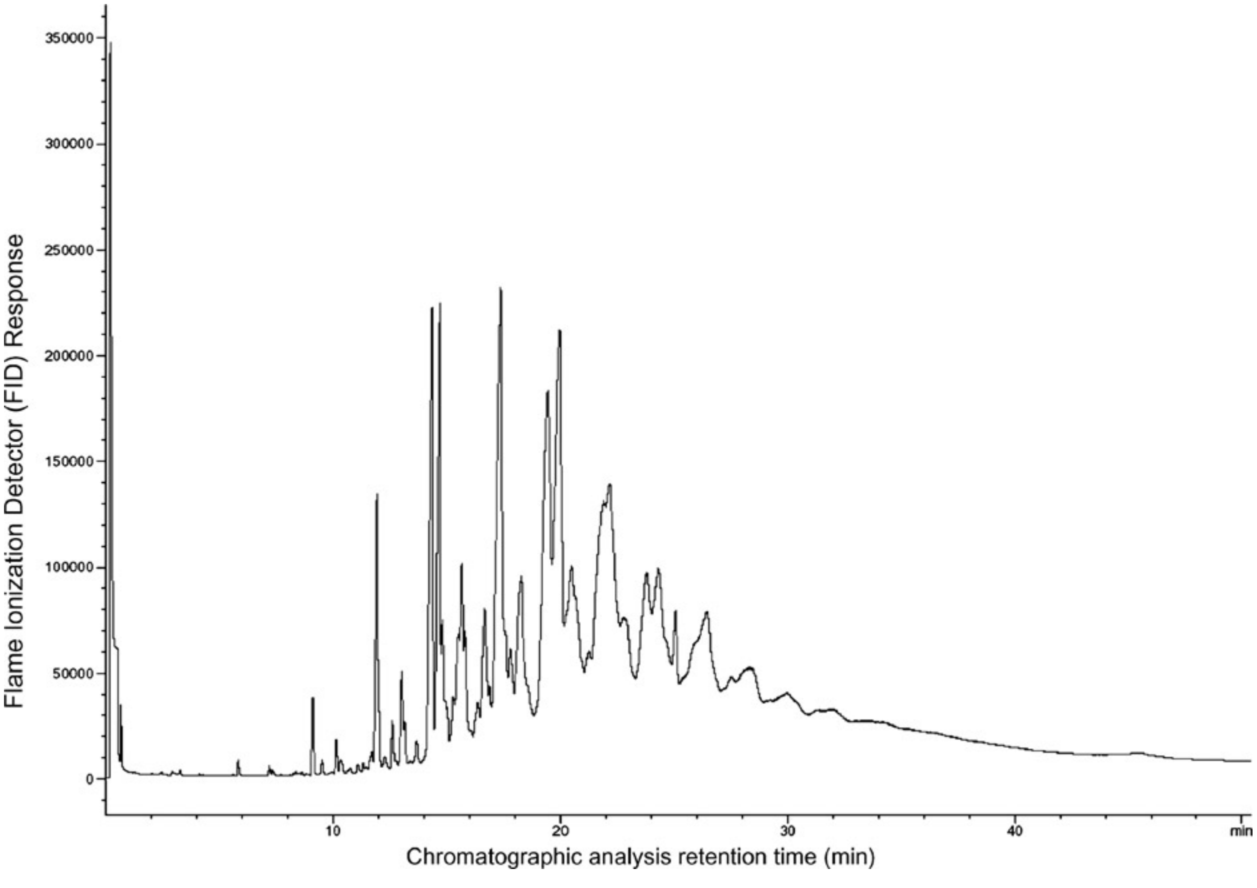

Figure 1. Hydrocarbon analysis result by HTSD for a contaminated sediment sample extract HC-S-19.

heavy HMW material may not be fully eluting and detected in the analysis.

The output from an HTSD analysis is illustrated in Figure 1 and Table 1. The instrumental response is provided as a chromatogram (detector response with time) of the sample analysis as shown in Figure 1. The tabulated report of the analysis gives the cumulative percentage hydrocarbon yield with approximate boiling point. The HTSD analysis determines the percent recovery of the detected hydrocarbon compounds in the sample compared to the weight of the sample injected into the instrument. The HTSD analysis is calibrated with a reference standard made from a distilled fraction from a crude oil. The recovery value determined is an approximate measure, for example, of oil or fuel product in the sample itself since the response factor of the reference material used to calibrate the method is not necessarily identical to that for the product actually present in the sample. The calculation of recovery is based on the response of the detector to the hydrocarbons in the calibration reference standard. The chromatographic time-temperature with n-paraffin carbon number calibration is established with a reference standard of normal paraffin hydrocarbons that includes carbon numbers in the C5 to C108 range.

A graphic representation of the incremental percentage of hydrocarbon material boiling at each carbon number and the cumulative sum percentage as the carbon number increases are shown in Figure 2. There are boiling point differences at a given carbon number for different types of hydrocarbons. The normal paraffins typically have higher boiling points than their isomers (isoalkanes) and lower boiling points than aromatics and alicyclic compounds for a given carbon number. Therefore, Figure 2 represents approximate carbon number as a function of boiling point distributions.

The GC-MS/NOISE method, as discussed earlier, is routinely used in our laboratory for determining hydrocarbon type distributions in various type samples from petroleum production and refining operations. More recently it has been applied to "fingerprinting" PAHs in environmental samples in efforts to determine the possible origin of hydrocarbons present.

This analytical method uses GC in tandem with MS based on nitric oxide reagent (as NO^+ ions) for chemical ionization (CI) of sample molecules. With this technique the most abundant reactions occur without cleaving carbon-carbon bonds in the parent molecule, which results in a more simplified mass spectrum with less molecular fragmentation. The specific reactions that occur are characteristic for the different hydrocarbon compound types, which allow their classification according to chemical functionality and number of carbon atoms in a molecule. In contrast, electron impact (EI) ionization conventionally uses higher

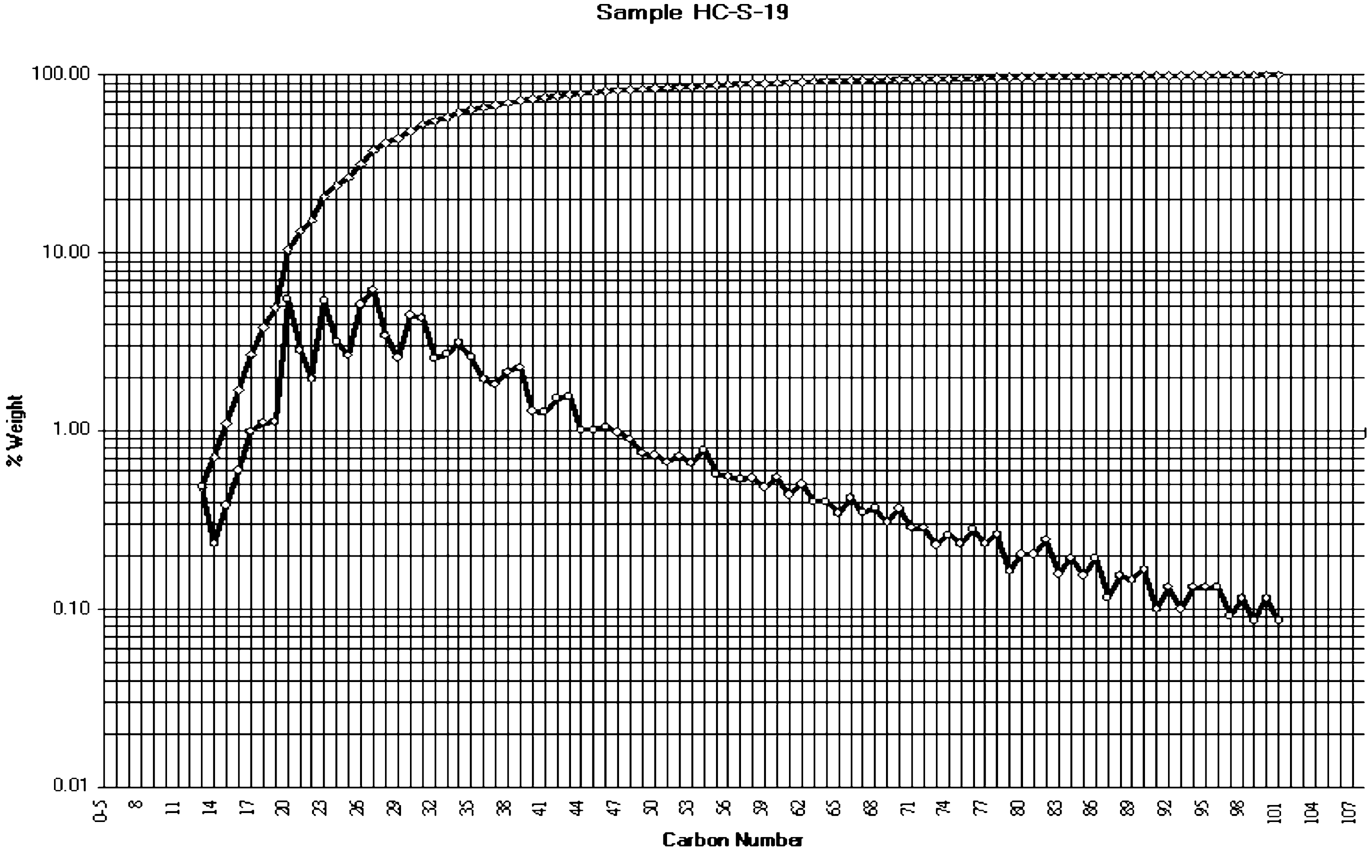

Figure 2. Carbon number report of the hydrocarbon yield (incremental and cumulative) by HTSD for a contaminated sediment sample extract.

energy than chemical ionization and results in more molecular fragmentation than CI. However, PAHs, unlike hydrocarbons such as alkanes and cycloalkanes, usually yield molecular ions by EI ionization.

The GC-MS/NOISE method, though typically not as sensitive as the GC-MS/Single Ion Monitoring (SIM) technique used in EPA Method 8270 (USEPA, 1996), showed good sensitivity for determining the PAH distributions in the application described in this article. The GC-MS/NOISE method is also advantageous in scanning for all hydrocarbon types in a sample analysis rather than for only specific targeted compounds.

Identification of End Members

In the evaluation of environmental samples that contain two or more possible hydrocarbon products, the goal is to identify the individual products, called end members. However, it should be pointed out that the true end members for a contaminated site are often not available. Also, because of boiling point pattern differences that may occur among products of the same generic type, such as bunker fuels, a particular generic end member product that is available for analysis may not be a sufficient match to material from the environmental sample. It may also be difficult to distinguish between particular products within the same generic type. Such occurrences can of course affect the accuracy of the techniques presented in this article.

Examples of the analysis of petroleum-derived (petrogenic) and combustion-derived (pyrogenic) products are illustrated to show the application of the presented analytical procedures. The HTSD chromatograms in Figure 3 show the boiling range patterns of typical petroleum-derived fuel products such as jet, diesel, and #6 fuel oil (bunker fuel). The #6 fuel oil contains a wider boiling range of hydrocarbons, which include relatively heavy materials. The HTSD chromatogram in Figure 4 shows the boiling range pattern of a combustion-derived pitch from coal tar sample. The GC-MS/NOISE analysis results in Figure 5 show a comparison of PAH distributions for a pitch from coal tar, #6 fuel oil, and a hydrocarbon-contaminated sediment sample extract. As discussed earlier, the skewed pattern of predominantly nonalkylated parent and 4-, 5-, and 6-ring PAHs are characteristic of pyrogenic hydrocarbons, as seen in the pitch from coal tar

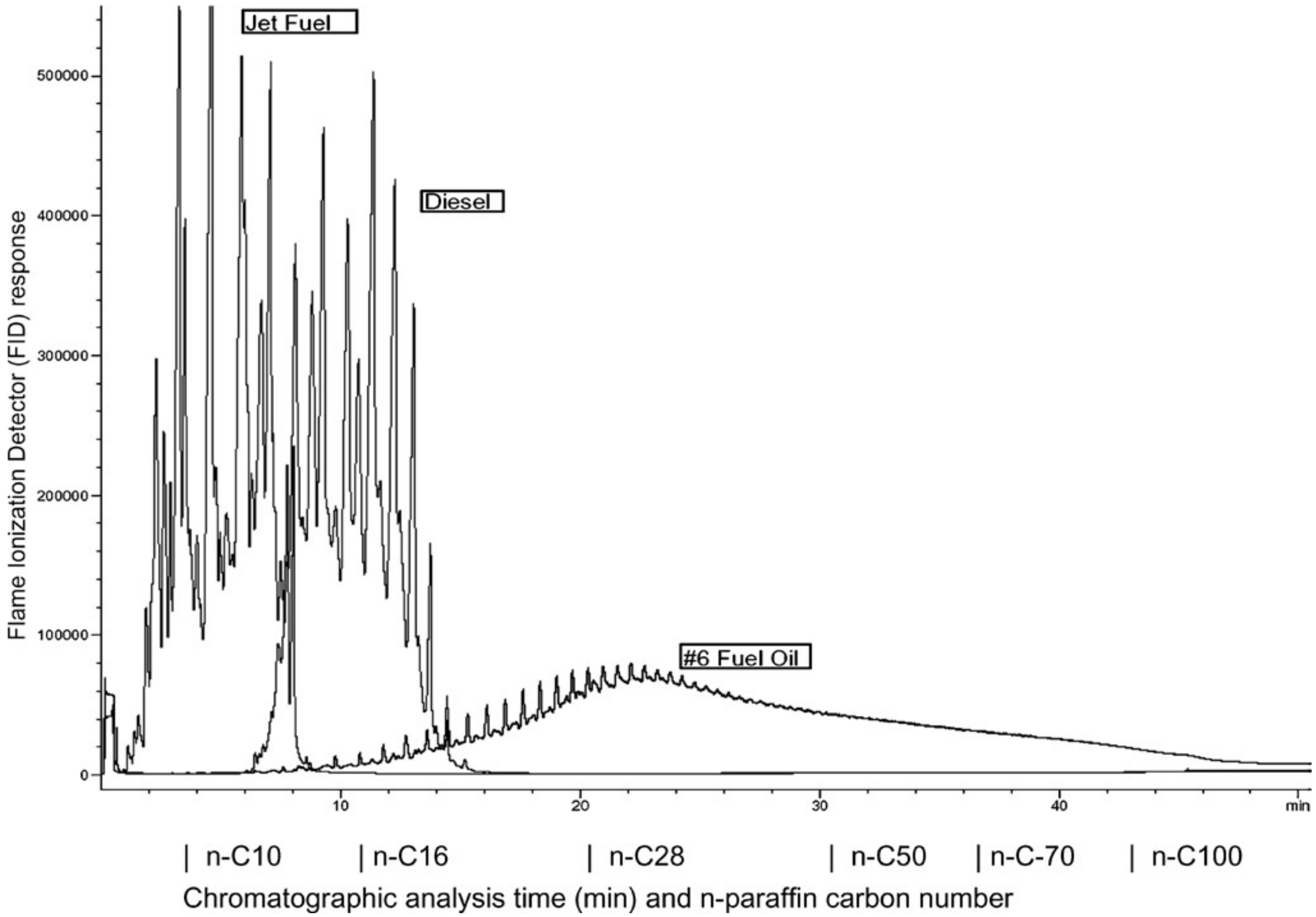

Figure 3. Hydrocarbon analysis patterns by HTSD analysis for samples of jet fuel, diesel fuel, and #6 fuel oil.

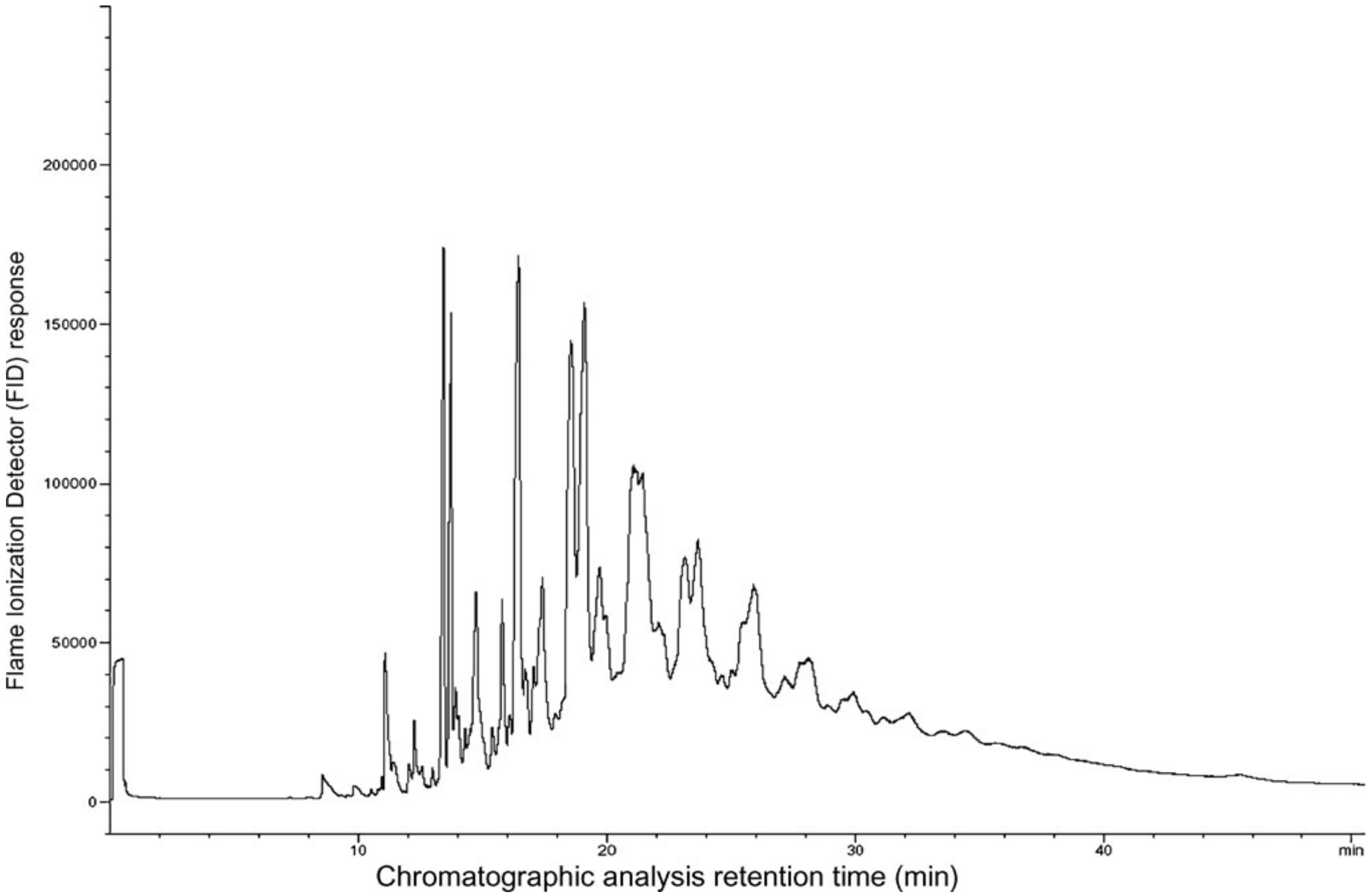

Figure 4. Hydrocarbon analysis result by HTSD analysis for a sample of pencil pitch from coal tar.

sample, while the bell-shaped pattern and predominately alkylated PAHs characteristic of petrogenic hydrocarbons are seen in the fuel oil sample. The sediment sample hydrocarbons are similar to petrogenic material. The determination of PAH distributions is valuable for determining the nature and possible source of hydrocarbons.

Determination of Sample Composition by HTSD and Percentage of End Members by Mathematical Regression

The value of the HTSD analysis protocol in this environmental application is twofold: it provides quantitative information over a wide range of the hydrocarbon spectrum, from about C15 to approximately C108 (loss of C5–C15 material is due to extraction solvent removal), and it provides quantitative information for individual components of the hydrocarbon mixture. These two advantages, combined with the use of mathematical regression to estimate the contribution of individual products in mixtures of hydrocarbons, provide the basis for a quantitative determination of the relative contribution of the components present in environmental samples.

The goal of the regression calculation presented here is to select the proportions of the two end members that best fit the actual sample yields as measured by HTSD within the appropriate carbon number range. The calculation procedure contains several steps and can be performed, for example, with Microsoft Excel (Microsoft Corporation) or an equivalent program and a standard “add-in” routine, for example, Microsoft Solver (Microsoft Corporation) or an equivalent.

Normalization of HTSD Data

The results of the HTSD analysis can be expressed on a normalized hydrocarbon recovery basis, which allows the boiling point distribution of hydrocarbons in all the samples to be compared on the same quantitative basis. Normalization removes the influence of material in the sample not determined in the HTSD analysis (for example, nonrecovered hydrocarbon residue material boiling higher than about C108, insoluble material, moisture), and any variations in the size of sample injected into the chromatograph.

Normalization also allows the scope of the method to alternatively be applicable for determining extractable and

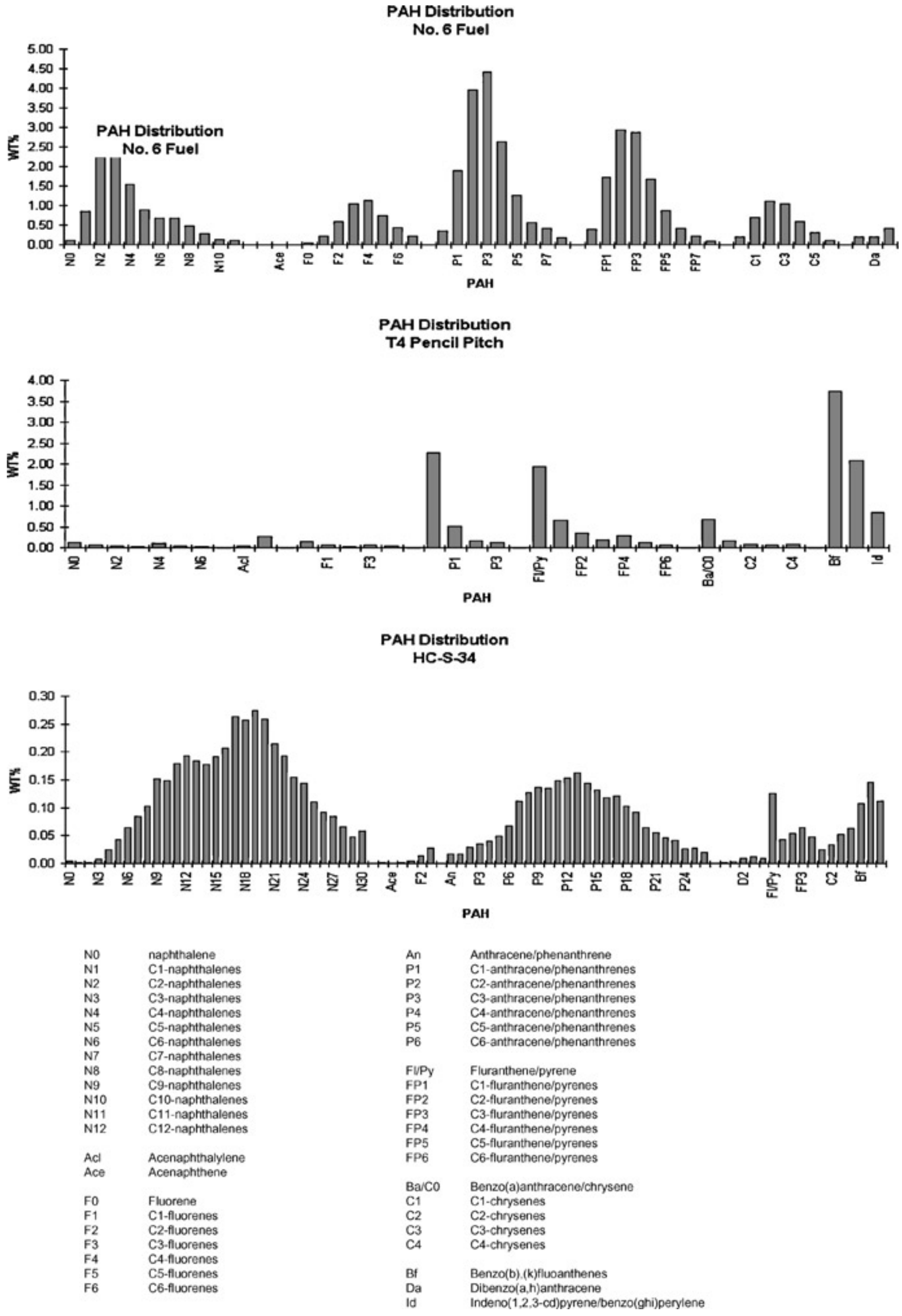

Figure 5. PAH distributions by GC-MS/NOISE technique for #6 fuel oil (bunker fuel), pencil pitch from coal tar, and hydrocarbon-contaminated sediment sample HC-S-34.

chromatographable hydrocarbon components in the carbon number range from about C5 to C108 if there were no need to perform the extraction gravimetric step.

Selection of Range of Hydrocarbons for Comparison

In the formulation of a procedure for evaluating the percentage of end members in a real-world sample, a range of molecular weights and carbon numbers must be considered. The end members, for example, can contain light ends subject to environmental modification and degradation through evaporative losses, solution in water, and biodegradation. Further, samples from the environment are potentially contaminated with "background" material from decaying plant matter and other anthropogenic sources.

In general, for the evaluation of the samples in the presented example application, the range of hydrocarbon molecular weights or carbon numbers from C30 through C50 were used.

Lighter components were eliminated due to possible losses from their volatility and water dissolution, and possible biodegradation and differing relative rates of biodegradation for each end member of the mixture. Heavier components—those with higher carbon numbers than C50—were eliminated due to possible background influences.

Mathematical Regression

HTSD data are expressed in terms of the hydrocarbon yield at each carbon number between C5 and C108. HTSD data for the two potential end members in this example, coal tar pencil pitch and bunker fuel, are placed in the same "data worksheet" as the data for the sample. Thus the worksheet data has the following content and arrangement:

Rows 1 to 4: Column identification information.
Column A: Carbon numbers from 5 through 108 in corresponding rows 5 to 108.
Column B: Sample yields by carbon number as generated directly from HTSD.
Column C: HTSD yields of the coal tar pencil pitch end member.
Column D: HTSD yields of the bunker fuel end member.

When the data entry is completed a series of calculations are performed. Another worksheet is created from the data in the "data worksheet," and in this "second worksheet" both the carbon number and the sample data columns are copied from the data worksheet to the same corresponding rows and columns (**A** and **B**). Next, the individual data values for the two end members are modified by multiplication by an *estimated* value (one each for the pencil pitch and bunker fuel) for the contribution of each end member to the sample. Thus every measured yield value for the coal tar pitch in the data worksheet is multiplied by a constant value and placed in the same corresponding column and row position (**C**) in the second worksheet. Likewise, the measured yield values for bunker fuel are multiplied by a constant value and placed in the same corresponding position (**D**) in the second worksheet. One can think of these initial constant values as representing the initially estimated proportions of the two end members in the sample that is some unknown mix of the two components.

With all these data in a spreadsheet, *Solver* (or equivalent) is then used to determine the best fit of some unknown proportions of bunker fuel and coal tar pitch in the sample. This is done by specifying that the sum of the absolute differences between the sample HTSD yields at each point, and the mathematical reconstruction based on the two end members, is a minimum. *Solver* is given the constraint that the multipliers of the two end members must not be negative, as this would not represent a physically possible situation. Carbon number ranges can also be specified (for example C30 through C50).

The use of only two potential end members is frequently not adequate to provide an acceptable match between the sample and the known contributors to the sample contamination. In such cases a residue or background is calculated that represents all other sources potentially contributing to contamination in the sample.

In order to visually check the validity of the Solver calculations, an overlay of the plot is made of the sample HTSD values and the calculated reconstruction. From this plot one can readily evaluate just how well the sample can be represented as a mix of the two end members. An example of the goodness of the

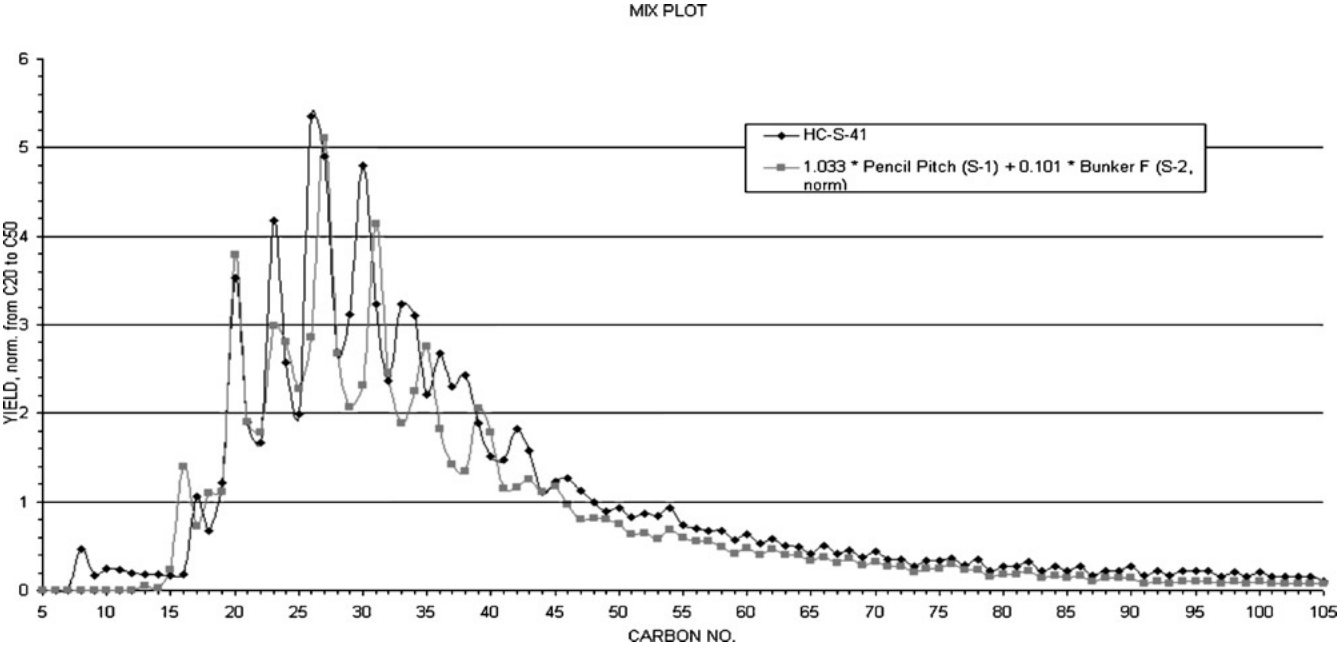

Figure 6. Graphic illustration of the goodness-of-fit between calculated values using regression analysis for a mixture of possible contaminant end member products and the actual chromatogram by HTSD analysis of a contaminated sediment sample HC-S-41.

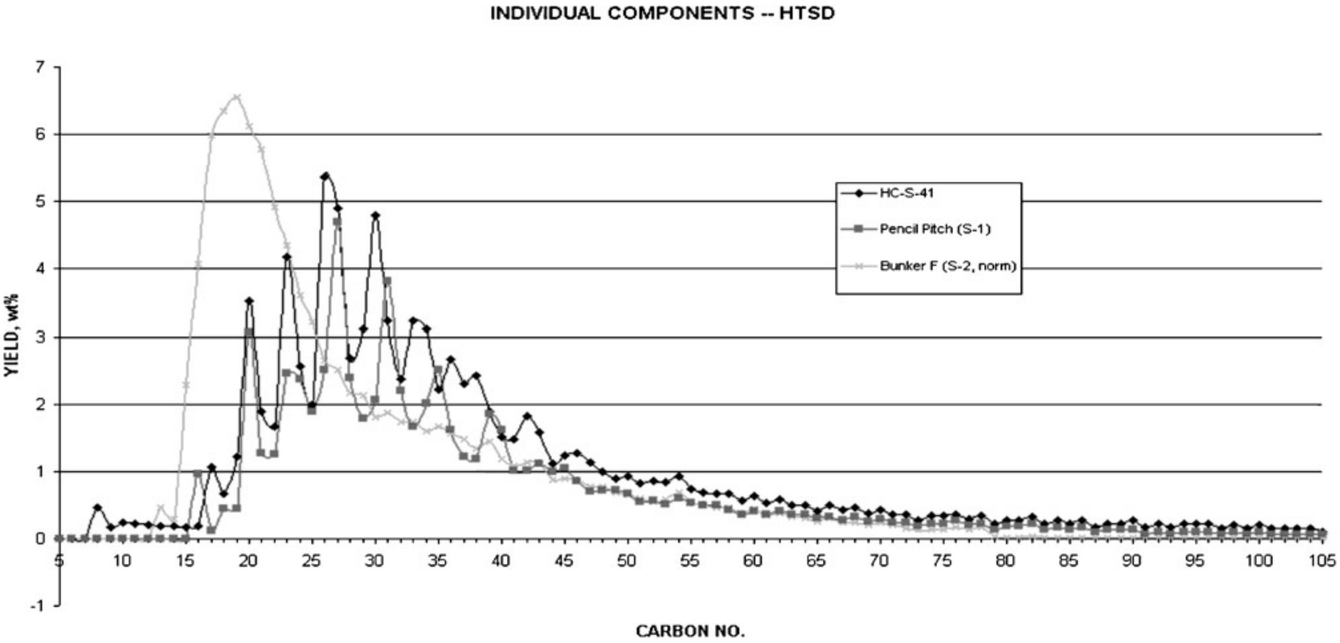

Figure 7. Graphic illustration of the HTSD analysis results for individual possible end member products and a contaminated sediment sample HC-S-41.

fit between the calculated values of the mixture and the actual analysis of a sediment sample (HC-S-41) is provided in the "Mix Plot" chromatograms in Figure 6. The HTSD analysis results for the individual potential end member products (pencil pitch and bunker fuel) and the sediment sample (HC-S-41) are shown in the Individual Components Plot in Figure 7.

In Figure 8, analysis results are shown for a different sediment sample (HC-S-34) for which the analytical data fits a predominantly bunker fuel product contribution to the hydrocarbon contamination in the sediment sample.

Application of Methods

Following the methodology presented above, sediment samples taken at various locations from a marine terminal slip were analyzed in our laboratory by HTSD, and the percentages of potential end member contaminants for the site (bunker fuel,

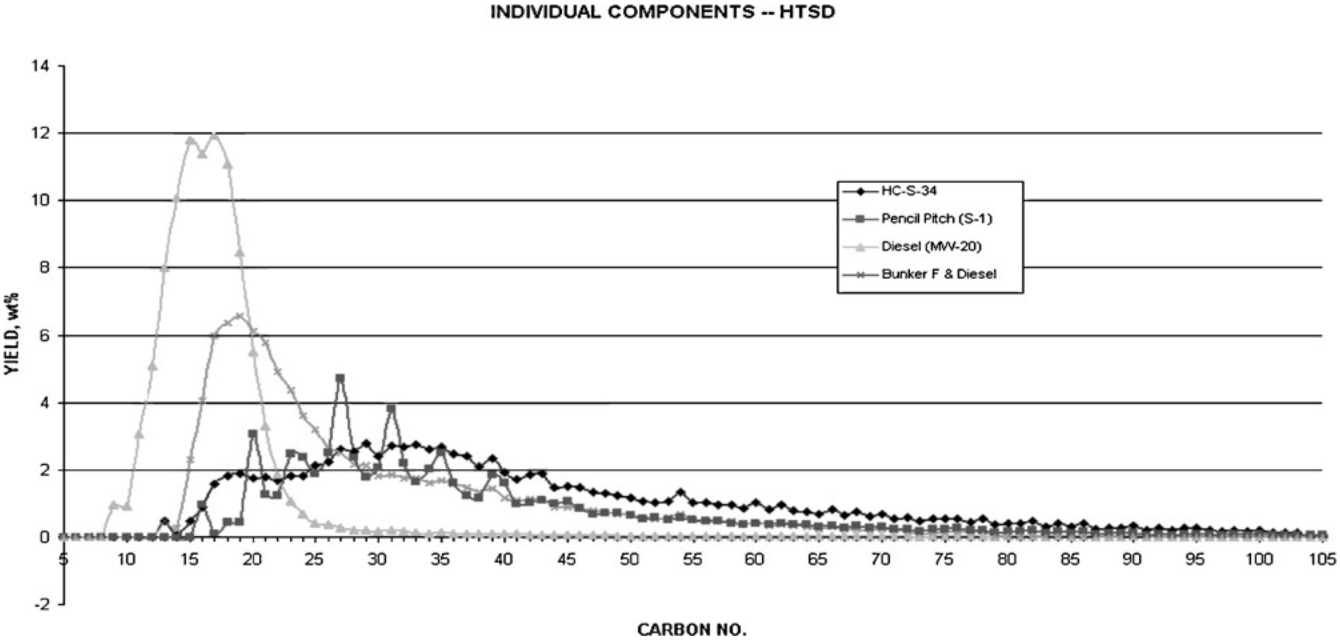

Figure 8. Graphic illustration of the HTSD analysis results for individual possible end member products and a sediment sample (HC-S-34) that fits a contamination from material in the boiling range of bunker fuel.

Table 2. *Analysis results for sediment samples*

	Carbon number range		Sample data			
Sample	From	To	Pencil pitch (S-1) (%)	Bunker fuel (%)	Residue (%)	HC by HTSD (ppmw)
HC-S-36	30	50	5	78	17	
HC-S-34	30	50	0	86	14	1976
HC-S-39	31	45	0	74	26	234
HC-S-40	30	50	0	83	17	308
HC-S-4	25	50	0	88	12	627
HC-S-3	25	50	61	33	6	1445
HC-S-38	25	50	55	39	6	3260
HCS-7	30	50	0	86	14	417
HCS-5	25	50	0	88	12	555
HCS-8	30	50	0	88	12	353
HC-S-22	20	50	74	19	7	
HC-S-26	30	50	0	84	16	
HC-S-31	20	50	91	0	9	
HC-S-36	30	50	42	54	4	
HC-S-41	20	50	74	10	17	
HC-S-42	20	50	80	8	12	
HC-S-43	20	50	63	27	10	
HC-S-00	30	50	0	88	12	
HC-S-12	31	50	37	63	0	
HC-S-18	20	50	70	21	9	
HC-S-19	31	50	58	42	0	
HC-S-20	20	50	68	24	8	
HC-S-21	20	50	72	18	10	

pencil pitch from coal tar, and residue or background material) were determined using the regression method outlined above. The results for the samples are presented in Table 2. The data show differing relative amounts of the potential end members for the different samples. For example, the results for sediment sample HC-S-41 show that the hydrocarbon contamination in the sample is a mixture of materials with chemical composition characteristics similar to coal tar pitch (74%), bunker fuel (10%), and a residue or background material (17%). On the other hand, sample HC-S-34 is shown by the analysis to contain predominantly bunker fuel (86%) and residue background material (14%). GC-MS/NOISE analysis of the HC-S-34 sample (as previously illustrated in Figure 5) confirmed a PAH distribution for this sample indicative of petrogenic material such as bunker fuel.

The analysis of the samples collected from the site indicated that the nature of the contamination present in the sediments represented mixtures in differing relative amounts of hydrocarbon materials with chemical compositional characteristics similar to coal tar pitch and bunker fuel. A residue or background material that represented all other sources of material detected was also indicated in most of the samples analyzed.

The hydrocarbon analysis data for the samples, their locations at the site, and other information that included historical usage and activities of the site indicated the contamination may have been derived from different sources, at different times, and by different entities.

Summary and Conclusions

A procedure is presented to characterize environmental samples that contain *mixtures of hydrocarbons* that may have arisen from materials that include fuels and other products used in commerce such as motor oil, bunker fuel, and heavier higher boiling products. The method can also be applicable for characterizing hydrocarbons from fuels such as gasoline, jet, and diesel as long as the analysis procedure used for extraction is performed in a manner that allows recovery of the lower boiling hydrocarbon components in those fuels. The procedure uses the analytical laboratory technique of HTSD and mathematical regression of the analytical data to estimate the relative contribution of individual products in mixtures of hydrocarbons present in environmental samples.

Also presented is an analytical technique to determine hydrocarbon-type distributions by GC-MS with nitric oxide ionization spectrometry evaluation. This analysis allows complex hydrocarbon mixtures to be classified by their chemical composition, or types of hydrocarbons that include paraffins, cycloparaffins, monoaromatics, and PAHs. The PAH distribution data is valuable for determining the nature and possible source of hydrocarbons in samples. These methods provide quantitative information and the boiling range of components of mixtures, as well as “hydrocarbon fingerprints” of the types of hydrocarbons present.

An example of an environmental application of the procedures is presented for sediment samples collected from a hydrocarbon-contaminated site. The analysis showed that the nature of the contamination present in these sediments represented mixtures of hydrocarbon materials with chemical compositional characteristics similar to coal tar pitch and bunker fuel. A residue or background material that represented all other sources of contamination detected was also indicated by the analysis. The relative contributions of coal tar pitch and bunker fuel to the contamination may have been derived from different sources, at different times, and by different entities. Discrimination between the contributions of end member materials in mixtures of hydrocarbon contamination can provide the basis for estimating the liability responsibilities of one party to two parties or multiple parties at contaminated sites.

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