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Oil Spill Source Identification by Comprehensive Two-Dimensional Gas Chromatography

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Comprehensive two-dimensional gas chromatography (GC × GC) with flame ionization detection has been applied to oil spill source identification. An oil spill case from the U.S. Coast Guard's Marine Safety Laboratories (MSL) was analyzed by GC × GC. A slightly weathered, marine diesel fuel spill sample was qualitatively and quantitatively compared to two potential source samples. The high resolving power of GC × GC separated several hundred components from the petroleum matrix. Compounds of similar chemical structure were grouped together in an ordered two-dimensional chromatogram. In these ordered groups, numerous small peaks representing minor components were separated and detected. This was especially helpful in determining compounds and compound classes to be used in the analysis. Several classes of compounds were found to be useful for comparing the samples, including alkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes, and anthracene/phenanthrenes. The GC × GC analysis resulted in a match between the spill sample and one of the source samples. This result was consistent with HRGC and GC/MS analyses employed by the MSL.

Introduction

Oil spilled in U.S. waterways is an area of continuing environmental concern. The U.S. Coast Guard has a statutory responsibility to respond to oil spilled on navigable waters (*1*). The Coast Guard Marine Safety Laboratories (MSL) utilize forensic oil analysis methods to help identify the party responsible for the spill. The majority of the spills analyzed by the MSL are less than 1000 gal and consist of petroleum distillate fuel oils or mixtures of oils spilled from vessels.

A multimethod approach to identifying the sources of unknown oil spills was developed and widely accepted during the 1970s (*2*). These early identification procedures used fingerprints from fluorescence and infrared spectra and gas chromatograms to visually compare and identify oil samples. Later, gas chromatography with mass spectrometry detection (GC/MS) was used for petroleum biomarker analysis, which led to enhanced oil identification (*3*). Hyphenated methods such as GC/MS provide information about specific chemical classes found within oil. Identification and comparison between compound classes, especially high molecular weight biomarkers, produce a more detailed and informative fingerprint. Presently, oil identification efforts rely heavily upon high-resolution capillary gas chromatography (HRGC) (*4*) and GC/MS (*5*) techniques. These methods may not always successfully differentiate similar light petroleum distillates because HRGC may not have the resolving power to detect minor components differences and the heavier GC/MS biomarkers may be absent in these products.

Our efforts to improve upon the present methods for oil spill source identification have focused on improving the resolving power of the chromatographic analysis. We have applied comprehensive two-dimensional gas chromatography (GC × GC) to oil spill source identification. GC × GC has a proven capability to separate complex mixtures, including petroleum. GC × GC has been successfully applied to the determination of pesticides extracted from human serum (*6*), oxygenates and BTEX in gasoline-contaminated groundwater (*7*) and to separate chemical classes in petroleum products (*8*−*10*).

GC × GC is well suited for petroleum analysis because it is capable of very high peak capacity (i.e., the number of peaks that can be resolved in a given time) or resolving power. Petroleum chromatograms generated under the conditions used in this study exhibit approximately 500 peaks. Under very high-resolution conditions, 4000 peaks have been produced (*11*). GC × GC is comprehensive because each analyte is subjected to two different separations. The two separations can be made to be orthogonal (*12*) so, in theory, the overall peak capacity is the product of the peak capacities of the two individual separations (*13*). Because GC × GC is orthogonal and comprehensive, it is considered a true multidimensional method.

GC × GC produces a two-dimensional retention plane that is much better for component identification than a single retention measure. Since GC × GC is an orthogonal separation, a component's position on the plane is dependent upon two independent fundamental molecular properties (e.g., volatility and polarity). Giddings referred to the fundamental molecular properties needed to separate all components of a mixture as dimensions (*14*). He postulated that when the separation method contained the same number and type of dimensions as the mixture, the multidimensional chromatogram would be ordered. GC × GC of petroleum produces ordered chromatograms when separated by volatility and polarity (*8*). Compounds of similar chemical structure are grouped together in the chromatogram. This grouping allows for rapid, preliminary identification. In these ordered groups, numerous small peaks representing minor components are separated and detectable.

The purpose of this study is to apply for the first time GC × GC analysis to source identification of marine oil spills. GC × GC chromatograms of spill and possible source samples were qualitatively and quantitatively compared to determine the source of the spilled oil.

Experimental Methods

Two-Dimensional Gas Chromatograph. The GC × GC system, shown in Figure 1a, consists of an HP 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE) configured with a thermal modulator assembly (Zoex Corp, Lincoln, NE) and a flame ionization detector (FID). The modulator configuration shown in Figure 1b includes two capillary

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TABLE 1. GC × GC Experimental Conditions

columns	retention gap	0.5 m × 0.100 mm deactivated fused silica
	first column	3.5 m × 0.100 mm with 3.0 μm (5% phenyl) methylsiloxane (Phase 007-2, Quadrex, New Haven, CT)
	modulator tube	0.15 m × 0.100 mm section of 3.5 μm dimethylpolysiloxane (Phase 007-1, Quadrex)/ 0.20 m ×0.100 mm deactivated fused silica
	second column	1.0 m × 0.100 mm with 0.14 μm ethylene glycol/siloxane copolymer (Phase 007-CW, Quadrex)
injection	split (50:1), 1.0 μL, 250 °C	
detector	FID 250 °C	
oven	50−250 °C, 4 °C min^{-1}	
flow	hydrogen, 0.5 mL min^{-1}, 63 cm s^{-1} at 50 °C	
modulator	ΔT = 100 °C, velocity 0.25 revolutions s^{-1}, period 5.0 s	

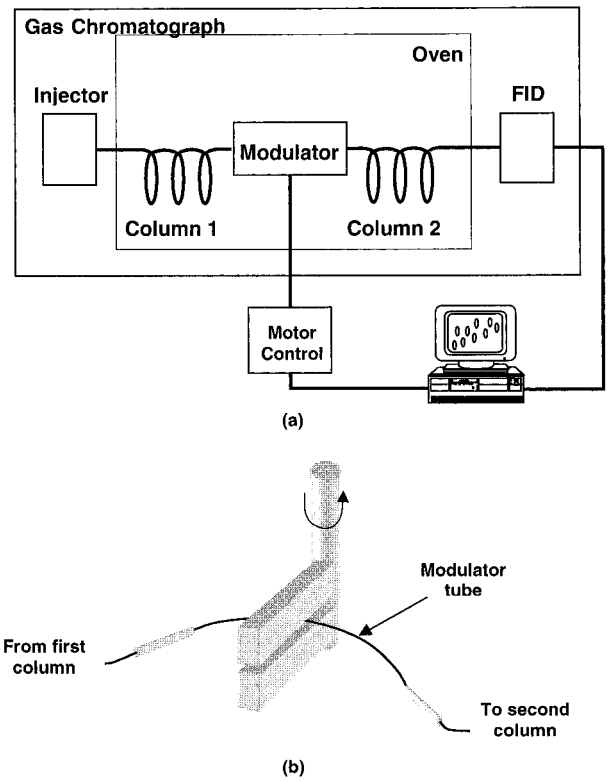

FIGURE 1. (a) Experimental system. (b) Modulator configuration showing the slotted heater position and motion relative to the modulator tube.

columns connected serially by the thermal modulator. The thermal modulator design and operation have been described elsewhere, so it will be explained here only briefly (*15*). The thermal modulator has two main components: a rotating slotted heater and a small section of capillary column called the modulator tube. The modulator tube is positioned at the interface between the two capillary columns. It is required to have an abrupt termination of stationary phase. This is accomplished by end-connecting a portion of phase-coated capillary column to a section of deactivated fused silica column. The slotted heater periodically rotates over the modulator tube to desorb, spatially compress, and inject portions of the first column eluent from the modulator tube into the second column. The heater is temperature-programmed to be approximately 100 °C above the oven temperature. Injection into the second column is very fast, on the order of 80 ms, and is suitable for fast GC on the second column. The heater movement and 80 Hz FID data collection are controlled with a PC running software written in LabView (National Instruments, Austin, TX). The GC × GC experimental conditions are listed in Table 1.

Two-Dimensional Chromatograms. In Figure 2, a small

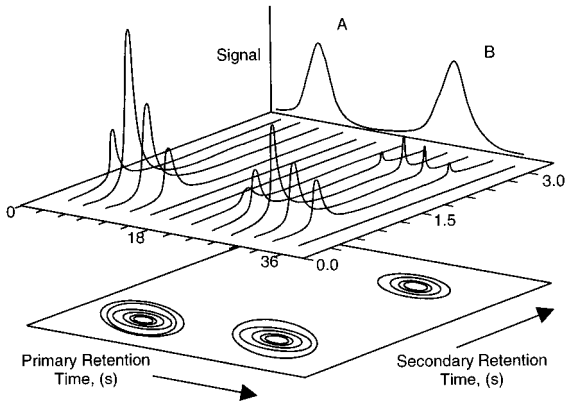

FIGURE 2. GC × GC data. A one-dimensional GC trace is on the backplane. Sequential GC × GC data traces are shown on the top plane. A contour plot of the GC × GC data appears as the bottom plane. Primary and secondary retention time axes are in seconds.

section of GC × GC chromatogram data is presented to illustrate how the FID data is extracted and assembled to generate a two-dimensional retention time plane. The primary retention time axis shows the chromatographic separation achieved by a nonpolar first column in the GC × GC. The backplane of the figure represents the resulting one-dimensional chromatogram. The width of the first dimension peaks are about 15−18 s, typical of one-dimensional chromatograms. The secondary retention time axis shows the chromatographic separation achieved by addition of a polar second column in a GC × GC analysis. The secondary chromatograms are 3 s long, contain 240 data points, and repeat every 3 s, the period of the modulator. The chromatography in the second column is fast, the peaks are typically 0.2 s in duration, and all the peaks are eluted before the successive chromatogram. Peak A contains a single component. At a modulation period of 3 s, the modulator will sample a 15-s peak eluting from the first column about 4 times. Thus, there will be four secondary chromatograms that contain that peak. It has been determined that about four secondary chromatograms are needed for each peak to preserve the resolution from the first dimension chromatogram (*16*). Peak B contains two components that are unresolved on the nonpolar first column stationary phase given their relative volatility and the chromatographic conditions employed. This peak is resolved into two components on the second column because of their difference in polarity. This demonstrates the significant advantage of a two-dimensional chromatographic approach over traditional one-dimensional methods for the analysis of complex mixtures. Furthermore, the figure demonstrates the comprehensive nature of GC × GC because all first column eluent is subjected to the second independent separation mechanism.

The plane below the chromatograms represents a contour plot of the GC × GC data. To facilitate visualization and

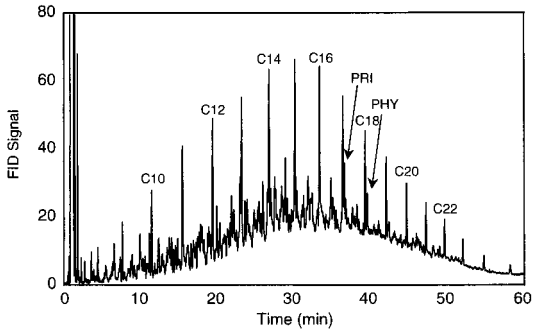

FIGURE 3. One-dimensional chromatogram of a marine diesel sample. The normal alkanes are labeled C(*n*) where *n* is the number of carbons. Two common isoprenoid biomarkers, pristane (PRI) and phytane (PHY), are also labeled.

analysis, chromatograms in this paper have the additional feature of interpolation between contours in accordance with a defined color palette. Low FID signals are colored white, medium are colored red, and high are colored dark blue. The baseline is colored light blue. The range of FID signals colorized has been reduced in order to visualize minor component peaks. This has the effect of chopping the top off of the tallest peaks, and these are a uniform light blue.

Oil Spill Samples. An oil spill case was selected from the U.S. Coast Guard Marine Safety Laboratory (MSL) in Groton, CT. The anonymous case included three samples. One sample designated Spill contained oil emulsified in saltwater. This sample was collected from the surface of the water approximately 24 h after an estimated 150-gal spill. Two additional samples designated Source 1 and Source 2 were neat marine diesel samples collected from the fuel tanks of two nearby suspect vessels.

The aqueous spill sample was extracted with cyclohexane, dried with anhydrous $MgSO_4$, and centrifuged to produce a cyclohexane solution with an unknown concentration of oil. The source samples were dried with $MgSO_4$ and then diluted to 5.0 μL of oil in 1.00 mL of cyclohexane solvent.

Results and Discussion

GC × GC Analysis of Oil Samples. Figure 3 is a one-dimensional chromatogram for a marine diesel sample obtained with only the nonpolar first column of the GC × GC. The normal alkanes from 8 to 23 carbons and oil biomarkers pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are prominent on the chromatogram. The hump in the middle of the chromatogram results from thousands of branched alkane, alkene, cycloalkane, and aromatic compounds, which are not chromatographically resolved.

Figure 4 is a portion of a volatility by polarity two-dimensional chromatogram for a marine diesel fuel sample. The chromatogram region between decane (C_{10}) and eicosane (C_{20}) is plotted to show greatest detail. The distribution of oil components across the nonpolar primary retention time axis correlates to the one-dimensional chromatogram in Figure 3; the oil components are sorted by volatility. The addition of the polar secondary retention time axis resolves many of the coeluters in Figure 3. In some second-dimension chromatograms, 10 coeluting peaks have been resolved. With the medium chromatographic resolution used in this experiment, over 500 individual peaks are observed in the GC × GC chromatogram. The chemical identities of some of these peaks are presently known and are listed in Table 2. These peaks have been identified by chemical standards, GC/MS data, or GC × GC with mass spectrometric detection (GC × GC/MS) (*17*).

The largest peaks present in the chromatogram are the homologous series of *n*-alkanes from 8 to 20 carbons running along the bottom of the chromatogram. This band appears at the bottom of the volatility by polarity chromatogram because the alkanes are the least polar oil components and have minimal retention on the polar second column. Other components in the bottom band lying between the *n*-alkanes are the branched chain alkanes that have similar polarity to, but different volatility than, the *n*-alkanes. Pristane and phytane are two examples of branched alkanes appearing in that band. Moving up the chromatogram, immediately above the alkane band is the one-ring and then the two-ring

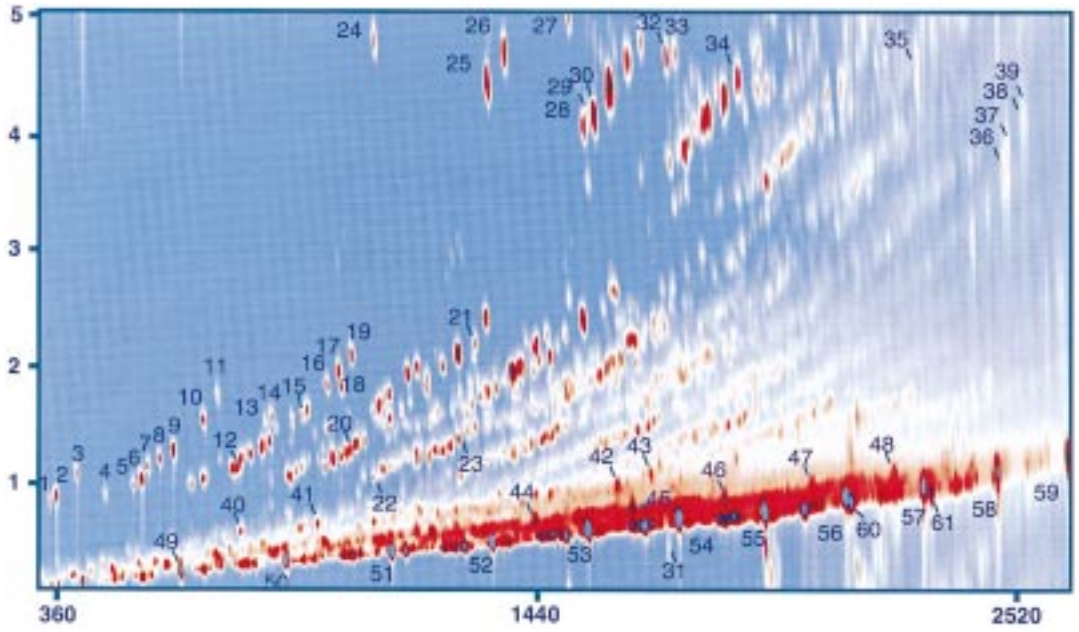

FIGURE 4. Portion of a volatility by polarity chromatogram for the same marine diesel sample shown in Figure 3. Both axes are in seconds. Peak identities are given in Table 2. Signal intensities are assigned a color from dark blue (high) through red (medium) to white (low). The baseline was colored blue to facilitate visualization. A small range of signal intensity is plotted so that the small peaks could be seen. The tallest peaks have been "chopped", resulting in the appearance of a uniform blue center.

TABLE 2. List of Compounds Identified in Figure 4[a]

peak no.	identity	family	CAS Registry No.
1	ethylbenzene	C2B	100-41-4
2	*m*-xylene/*p*-xylene	C2B	108-38-3/106-42-3
3	*o*-xylene	C2B	95-47-6
4	isopropylbenzene	C3B	98-82-8
5	propylbenzene	C3B	103-65-1
6	1-ethyl-3-methylbenzene/1-ethyl-4-methylbenzene	C3B	620-14-4/622-96-8
7	1,3,5-trimethylbenzene	C3B	108-67-8
8	1-ethyl-2-methylbenzene	C3B	611-14-3
9	1,2,4-trimethylbenzene	C3B	95-63-6
10	1,2,3-trimethylbenzene	C3B	526-73-8
11	indan	C3B	496-11-7
12	*n*-butylbenzene	C4B	104-51-8
13−14	methylindan[b]	C4B	
15	1,2,4,5-tetramethylbenzene	C4B	95-93-2
16−17	methylindan[b]	C4B	
18	1,2,3,4-tetramethylbenzene[b]	C4B	488-23-3
19	tetrahydronaphthalene	C4B	119-64-2
20	*n*-pentylbenzene	C5B	538-68-1
21	pentamethylbenzene	C5B	700-12-9
22	1,4-diisopropylbenzene	C6B	100-18-5
23	*n*-hexylbenzene	C6B	1077-16-3
24	naphthalene	N	91-20-3
25	2-methylnaphthalene	C1N	91-57-6
26	1-methylnaphthalene	C1N	90-12-0
27	biphenyl[b]	BP	92-52-4
28	2-ethylnaphthalene	C2N	939-27-5
29	1-ethylnaphthalene	C2N	1127-76-0
30	2,6-dimethylnaphthalene	C2N	581-42-0
31	1,8-dimethylnaphthalene	C2N	569-41-5
32−33	methylbiphenyl[c]	C1BP	
34	2,3,5-trimethylnaphthalene	C3N	2245-38-7
35	anthracene/phenanthrene	AP	
36−39	methylanthracene/phenanthrene[b]	C1AP	
40	*trans*-decahydronaphthalene	CA	493-02-7
41	*cis*-decahydronaphthalene	CA	493-01-6
42−43	pentamethyldecahydronaphthalene[c]	CA	
44	*n*-heptylcyclohexane[c]	CA	5617-41-4
45	*n*-octylcyclohexane[c]	CA	1795-15-9
46	*n*-nonylcyclohexane[c]	CA	2883-02-5
47	*n*-decylcyclohexane[c]	CA	1795-16-0
48	*n*-undecylcyclohexane[c]	CA	54105-66-7
49	decane	A	124-18-5
50	undecane	A	1120-21-4
51	dodecane	A	112-40-3
52	tridecane	A	629-50-5
53	tetradecane	A	629-59-4
54	pentadecane	A	629-62-9
55	hexadecane	A	544-76-3
56	heptadecane	A	629-78-7
57	octadecane	A	593-45-3
58	nonadecane	A	629-92-5
59	eicosane	A	112-95-8
60	pristane	IA	1921-70-6
61	phytane	IA	

[a] All compound identities are based upon the use of standards unless noted. [b] Compound identified using GC/MS. [c] Compound identified using GC × GC/MS.

cycloalkane band. Two components in these bands, *cis*- and *trans*-decahydronaphthalene, have been identified using standards. Several *n*-alkylcyclohexanes have been tentatively identified using GC × GC/MS. It is suspected that these bands also contain alkenes, although we have not confirmed their presence with standards or mass spectra.

The most noticeable aspect of the chromatogram is the many linear bands of compounds that begin just above the cycloalkane/alkene band and continue upward. These are populated primarily by aromatics. Each band contains an aromatic family in which a fundamental aromatic structure (e.g., benzene, naphthalene) has a specific number of attached carbons. For example, there are nine members of the three-carbon-substituted benzene family (C3B), and they all form a linear band containing eight resolved peaks. The eight structural isomers of propylbenzene with the chemical formula C_9H_{12} are present. They elute by boiling point starting with isopropyl benzene and ending with 1,2,3-trimethylbenzene. Two isomers, 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene, coelute in both dimensions, so they appear in the chromatogram as one peak. The peak at the right end of the band is indan, the ninth member of the C3B family, with the chemical formula C_9H_{10}. Analysis of the C4B band shows a structural isomer sequence very similar to the C3B band. The least substituted, lowest boiling point benzenes are located early in the band, and the tetra-substituted benzenes are late in the band. The C4B band terminates with tetrahydronaphthalene, a homologue of indan with one

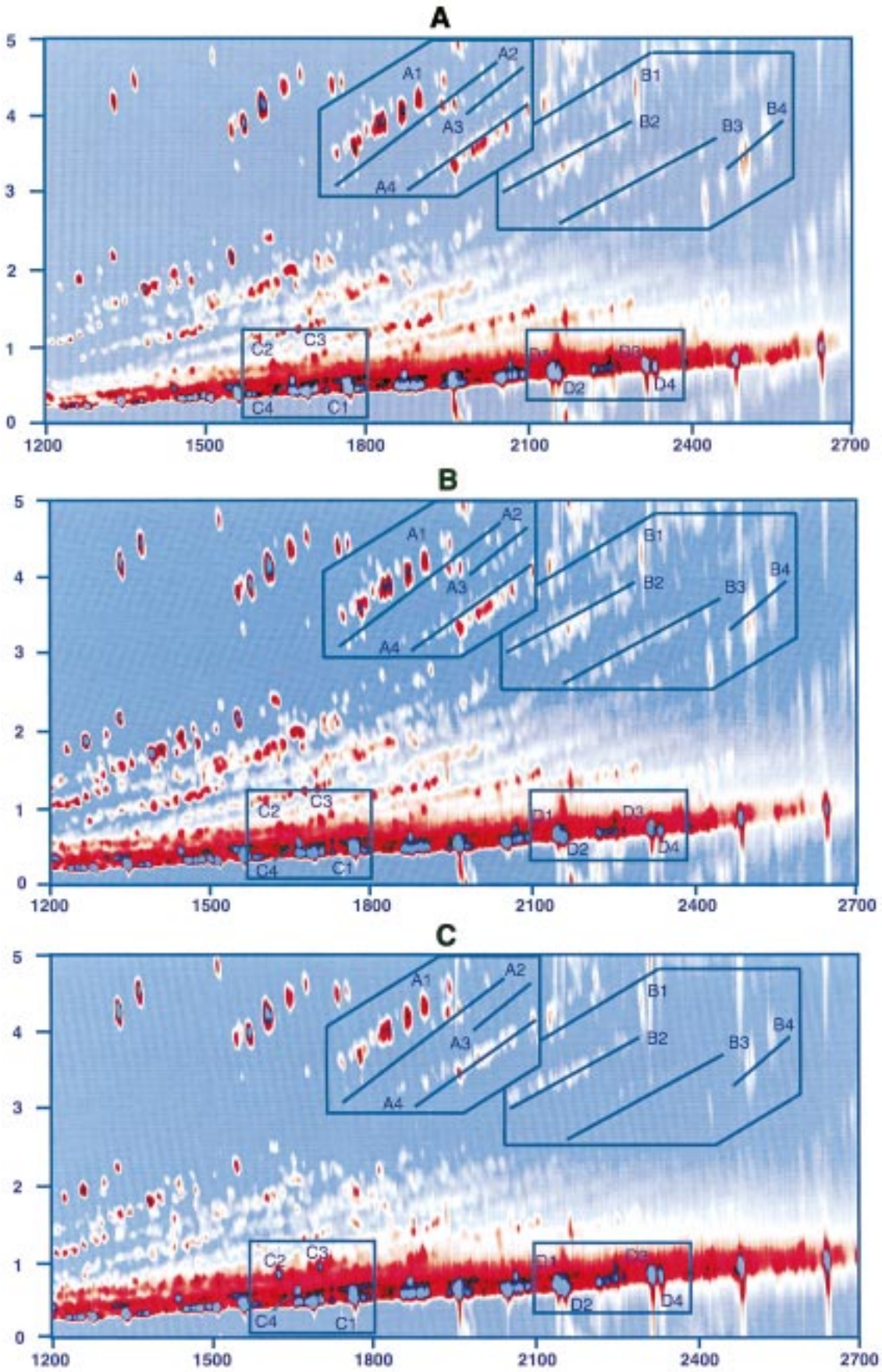

FIGURE 5. Portion of the volatility by polarity chromatogram from each of three samples analyzed. The spill sample is shown in panel A; one potential source, Source 1, is shown in panel B; and one potential source, Source 2, is shown in panel C. Both axes are in seconds. Each chromatogram is visualized using the same criteria to facilitate direct comparison. The boxes contain chemical families and individual compounds used to quantitatively compare each potential source sample with the spill sample.

additional carbon on the saturated ring. A distance approximated by the distance between nonane (C_9) and decane (C_{10}) separates indan and tetrahydronaphthalene spatially in the chromatogram. This relationship between chemical structure and position on the retention time plane produces a logical chemical interpretation of chromatograms and is an important benefit of GC × GC.

Benzene bands identified by standards in this chromatogram span from the two-carbon-substituted benzene (C2B) band at the left through the six-carbon-substituted benzene (C6B) band containing numerous structural isomers near the middle of the chromatogram. Bands appearing to the right of C6B likely result from even greater carbon substitution on benzene. By exploiting the repeating nature of these bands, the family of aromatic isomers responsible for each band can be identified even though the individual identities of the peaks are not known.

Repeating band structure is also visible for naphthalene and anthracene/phenanthrene components. Naphthalene (N) through the three-carbon-substituted naphthalene (C3N) bands have been identified with standards. The C4N through C7N are also identified based on the chemical logic of repeating bands. A peak for unresolved anthracene and phenanthrene (AP) and a band for one-carbon-substituted anthracene/phenanthrene (C1AP) have been identified. These compounds are more polar (and thus more strongly retained on the polar second column) than either the benzenes or naphthalenes, so their bands are expected at greater second-dimension retention time. However, their retention exceeds the 5 s modulator period of the GC × GC, so these components are wrapped onto the subsequent second-dimension chromatogram and have an apparent shorter retention.

The aromatics are the focus of this study because they are particularly useful for identifying and distinguishing oil samples. We can select from a variety of stationary phases for the first and second dimension to optimize the separation for particular bands of oil components. The columns used in this experiment are particularly suited for resolving and ordering the aromatic bands in the oil sample.

Oil Spill Case. The goal of oil spill case analysis is to determine the similarities and differences between the spill and possible sources. GC × GC chromatograms of the Spill, Source 1, and Source 2 are shown in Figure 5A−C. Each chromatogram is an enlargement of a selected region from about tridecane (C_{13}) to eicosane (C_{20}) that contains features found suitable for source determination. This higher boiling point region is more suitable because the Spill sample showed weathering, resulting in a loss of compounds eluting before dodecane (C_{12}). Weathering by evaporation and dissolution occurred because the spill was on the water approximately 24 h prior to sampling. Each sample was compared to the spill qualitatively by visual comparison and quantitatively by integration of selected peaks and bands.

Visual comparisons between the spill and source chromatograms in Figure 5 were made with respect to the presence or absence of peaks at a particular location on the retention time plane and their relative size. Each source sample exhibited both similarities and differences when compared to the spill sample. The majority of the features in each of the oil sample chromatograms are similar. The alkane range is the same in all samples. The substituted benzene, naphthalene, and anthracene/phenanthrene bands appear in all samples. These macroscopic similarities result from the fact that all of the oil samples are the same oil type, specifically marine diesel fuel. However, small differences between the sample chromatograms are immediately visible. For example, Source 2 exhibits considerably fewer peaks in the heavy aromatic region than the Spill.

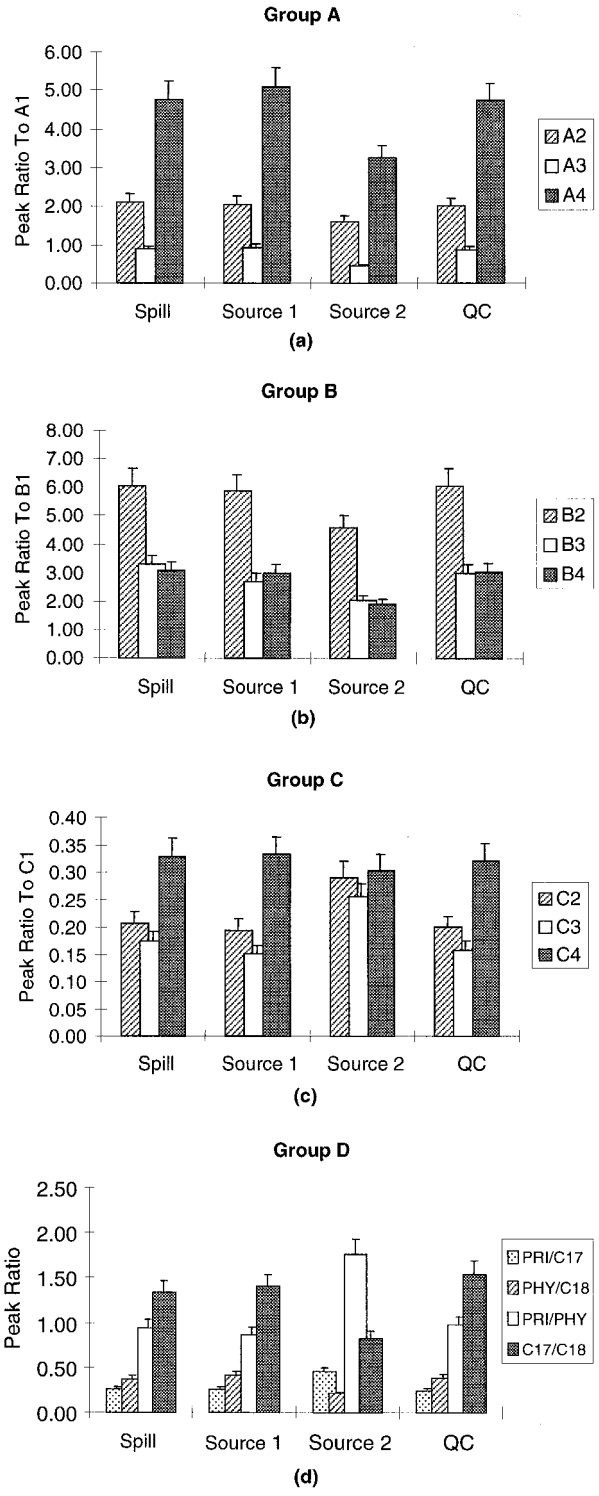

FIGURE 6. Quantitative comparisons between the spill sample and the two potential source samples. A quality control sample (QC), split from the spill sample, was also analyzed. Each panel represents the results of integrating peaks within an individual box shown in Figure 5. Each bar represents the total peak or band volume ratioed to the first peak in the box. The error bar represents an estimated 10% variation in results but is shown only in the plus direction. Compound classes represented: panel a, alkylnaphthalene bands ratioed to 2,3,5-trimethylnaphthalene; panel b, alkylanthracenes and alkylphenanthrenes ratioed to anthracene/phenanthrene; panel c, cycloalkanes ratioed to pentadecane; panel d, heptadecane (C17), octadecane (C18), pristane (PRI), and phytane (PHY) ratioed to each other.

Each chromatogram in Figure 5 is overlaid with four windows that highlight regions that will be compared to quantitate the similarities and differences between these oil samples. Selected peaks and bands within these windows were integrated and normalized to a specific peak within the area to quantitate relative amounts for comparison between samples.

Window A focuses on naphthalene components because they are prevalent in petroleum products, are resistant to evaporative weathering, and are known to exhibit variation useful for fingerprinting. Peak A1 is 2,3,5-trimethylnaphthalene, a resolved three-carbon-substituted naphthalene (C3N). The A4 band is known to be four-carbon-substituted naphthalenes (C4N); the A2 and A3 band components are not identified but are related in volatility and polarity to the substituted naphthalene components. The integration results of bands A2−A4 are shown in Figure 6a. Each band integration was normalized to A1. The data labeled quality control (QC) is a repetitive analysis of the Spill sample. The uncertainty in the integrated peaks, conservatively estimated from a previous quantitation study (*7*), is 10% and is indicated by the error bars on the bar graph. The bar graphs indicate that Source 1 and the Spill are similar, while Source 2 and the Spill are different.

Window B focuses on anthracene/phenanthrene components because they possess fingerprinting properties similar to naphthalenes. Peak B1 is anthracene and phenanthrene, which coelute under the conditions employed in this study. The B2 band contains five-carbon-substituted naphthalenes (C5N), and the B3 band are C6Ns. The B4 band contains one-carbon-substituted anthracenes or phenanthrenes. The integration results of bands B2−B4 are shown in Figure 6b. Each band integration was normalized to B1. The bar graphs indicate that Source 1 and the Spill are similar, while Source 2 and the Spill are different.

Window C contains alkane and cycloalkane components. These compounds are rarely used in traditional methods for fingerprinting, but differences observed in GC × GC chromatograms suggest they may be capable of discriminating between similar samples. Peak C1 is pentadecane. Mass spectral information was used to tentatively identify C2 and C3 as two isomers of pentamethyldecahydronaphthalene and C4 as *n*-octylcyclohexane. The integration results of peaks C2−C4 are shown in Figure 6c. The peak integration was normalized to C1. The bar graphs indicate that Source 1 and the Spill are similar, while Source 2 and the Spill are different.

Window D has four labeled peaks, D1−D4. D1 is *n*-heptadecane, D2 is pristane, D3 is *n*-octadecane, and D4 is phytane. There are four different ratio combinations between these four peaks that are traditionally used by scientists to discriminate between oil samples. Bar graphs of these ratios are presented in Figure 6d. The bar graphs indicate that Source 1 and the Spill are similar, while Source 2 and the Spill are different.

On the basis of qualitative and quantitative results, Source 1 was determined to be a probable match with the spill. These results are consistent with the conclusions of the USCG MSL, who employed HRGC (*4*) and GC/MS (*5*) analyses to determine the source of the spill.

The work described here represents the first known application of GC × GC to oil spill source identification. The high resolving power of GC × GC resulted in differentiation of two similar marine diesel fuels using both major and minor components of varying chemical class. Future work will include the analysis of weathered and biodegraded samples, comparison of different petroleum products, and direct comparison between GC × GC and GC/MS methods.

Acknowledgments

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Literature Cited

(1) Protection of the Environment. *Code of Federal Regulations*, Title 40, Part 300; U.S. Government Printing Office: Washington, DC, 1997.
(2) Bentz, A. P. *Anal. Chem.* **1976**, *48*, 454A−472A.
(3) Albaiges, J.; Albrecht, P. *Int. J. Environ. Anal. Chem.* **1979**, *6*, 171−190.
(4) *Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography*; D-332890; American Society for Testing and Materials: Philadelphia, 1990.
(5) *Standard Practice for Oil Spill Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometery;* D-5739-95; American Society for Testing and Materials: Philadelphia, 1990.
(6) Liu, Z.; Sirimane, S. R.; Patterson, D. G.; Needham, L. L. *Anal. Chem.* **1994**, *66*, 3086−3092.
(7) Gaines, R. B.; Ledford, E. B.; Stuart, J. D. *J. Microcolumn Sep.* **1998**, *10*, 597−604.
(8) Ledford, E. B.; Phillips, J. B.; Xu, J.; Gaines, R. B.; Blomberg, J. *Am. Lab.* **1996**, *28*, 22−25.
(9) Phillips, J. B.; Venkatramani, C. J. *J. Microcolumn Sep.* **1993**, *5*, 511−516.
(10) Blomberg, J.; Schoenmakers, P. J.; Beens, J.; Tijssen, R. *J. High Resolut. Chromatogr.* **1997**, *20*, 539−544.
(11) Phillips, J. B.; Xu, J. *J. Chromatogr. A* **1995**, *703*, 327−334.
(12) Venkatramani, C. J.; Xu, J.; Phillips, J. B. *Anal. Chem.* **1996**, *68*, 1486−1492.
(13) Giddings, J. C. In *Multidimensional Chromatography*; Cortes, H. J., Ed.; Marcel Dekker: New York, 1990; Chapter 1.
(14) Giddings, J. C. *J. Chromatogr. A* **1995**, *703*, 3−15.
(15) Phillips, J. B.; Gaines, R. B.; Blomberg, J.; van der Wielen, F. W. M.; Dimandja, J.; Greene, V.; Granger, J.; Patterson, D.; Racovalis, L.; de Geus, H.-J.; de Boer, J.; Haglund, P.; Lipski, J.; Sinha, V.; Ledford, E. B. *J. High Resolut. Chromatogr.* **1999**, *22*, 3−10.
(16) Murphy, R. E.; Schure, M. R.; Foley, J. P. *Anal. Chem.* **1998**, *70*, 1585−1594.
(17) Frysinger, G. S.; Gaines, R. B. *J. High Resolut. Chromatogr.* In press.

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