A Comprehensive Two-Dimensional Gas Chromatography Method for Analyzing Extractable Petroleum Hydrocarbons in Water and Soil

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Abstract

A flow-switching two-dimensional gas chromatography (GC×GC) apparatus has been constructed that can operate at temperatures as high as 340°C. This system is employed to analyze complex hydrocarbon mixtures such as diesel fuel, gas-oil, motor oil, and petroleum contaminated environmental samples. The GC×GC system generates two-dimensional chromatograms with minimal overlap between the aliphatic and aromatic regions. This allows these compound classes to be independently quantitated without prior fractionation. The GC×GC system is used to analyze extracts of spiked water samples, wastewater, and soil. The accuracy of the method is compared to that of the Massachusetts Extractable Petroleum Hydrocarbons (MA EPH) method. The GC×GC system generates a quantitative accuracy similar to the MA EPH method for the analysis of spiked water samples. The GC×GC method and the MA EPH method generate comparable levels of total hydrocarbons when wastewater is analyzed, but the GC×GC method detects a significantly higher aromatic content and lower aliphatic content. Both the GC×GC method and MA EPH method measure comparable levels of aromatics in the soil samples.

Introduction

Leakage of materials from underground petroleum storage tanks has generated significant concern over the last ten years. Many agencies, groups, and states in the U.S. have developed methodologies to analyze the extractable petroleum hydrocarbons (EPHs) in water and soil samples. The Massachusetts Extractable Petroleum Hydrocarbons (MA EPH) method developed by the Massachusetts Department Environmental Protection is the most broadly adopted. EPH methods provide quantitative estimates of the aliphatic, aromatic, and polycyclic aromatic hydrocarbon (PAH) content of petroleum-contaminated water and soil samples.

Single-column gas chromatography is incapable of separating the aliphatic and aromatic classes. Thus, a two-step approach has been adopted. (*i*) The hydrocarbons are first separated into aliphatic and aromatic fractions using silica solid-phase extraction (SPE) cartridges. (*ii*) The fractions are then individually characterized with gas chromatography–flame ionization detection (GC–FID). Unfortunately, the success of the fractionation depends on the uniformity of commercial silica SPE cartridges and reagents. Variability of the fractionation medium and/or reagents often results in the breakthrough of target compounds into the wrong fraction and/or contamination of the final extracts. Other criticisms of this method include high cost, long analysis time, and overly lenient acceptance criteria.

This article describes the evaluation of a valve-based comprehensive two-dimensional gas chromatography (GC×GC) method to replace both the SPE fractionation and GC–FID analysis steps. GC×GC has been shown to be an effective approach for analyzing petroleum mixtures (2–21). The vast majority of the published GC×GC petroleum separations have employed thermal modulation (2–4,6–12,15,17,19,22). A recent study by Van De Weghe et al. (23) has shown that thermal modulation GC×GC can produce group-type separations of oil-contaminated soil. GC×GC was compared to the standard SPE fractionation/single-column GC method and excellent agreement was observed. Thermal modulation GC×GC systems provide unsurpassed resolution, but often require the use of extensive amounts of cryogenic fluids.

Valve-based modulation has been developed over the past ten years. Initial designs passed the sample through multi-port valves (16,24–26). The diaphragm valves used in many of these studies (24,25) have an upper temperature limit of 200°C. This constrained valve-based GC×GC to the analysis of relatively volatile samples. A series of fluidic modulators have been recently developed that do not place any temperature-sensitive parts in the sample path (13,18,20,21,27,28). The portion of the modulator that is in contact with the sample is constructed with thermally-robust components such as chromatography unions and conduits. The temperature sensitive solenoid valve-switching mechanism does not contact the sample and is placed outside the chromatography oven. Thus, the temperature limit of fluidic modulation strategies is constrained by the upper temperature limits of the unions and conduits. These limits are normally higher than the upper temperature limits of commonly employed stationary phases. Previous studies have shown that valve-based fluidic modulators can be used to provide qualitative

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and quantitative analyses of a variety of fuel samples, including gasoline (18,20,21), diesel (13), and biodiesel blends.

In order for valve-based GC×GC analysis to replace the SPE fractionation and GC–FID analyses used in most EPH methods, it must be capable of: (*i*) separating the aliphatic and aromatic classes and (*ii*) withstanding the high temperatures required to elute aliphatics up to C_{36} and PAHs as large as benzo[ghi]perylene ($C_{22}H_{12}$). This will most likely involve separation temperatures in excess of 300°C. Such high temperatures constrain the choice of stationary phases and fluidic components that can be used. This article describes the use of temperature-robust columns and a one-piece microfluidic Dean's switch modulator. The low number of tubing connections in this modulator greatly reduces the likelihood of leakage resulting from the thermal expansion and contraction of fitting components.

Experimental

GC×GC apparatus

An Agilent 6890 (Agilent Technologies, Inc., Wilmington, DE) fitted with an Agilent Microfluidic Dean's switch served as the GC×GC instrument. This apparatus has been described in detail in a previous study (21) and is shown in Figure 1. Liquid samples were introduced in 1 µL quantities through a cool-on-column inlet temperature set at 3°C above the oven temperature. A 1 m × 0.32-mm fused silica guard column was used upstream of the primary column. Two sets of columns and temperature programs were tested (see Table I). The DB-1, DB-1HT, DB-17HT columns were manufactured by Agilent, while the ZB-50 column was manufactured by Phenomenex (Torrence, CA). Comparable results were obtained with both column sets. Hydrogen was used as a carrier gas with a primary flow of 1 mL/min and secondary flow of 10 mL/min split evenly between the 2° column and a flow restrictor of the same dimensions. The pneumatics were operated in constant flow mode. The DB-17HT × DB-1 column set had 95 kP_a primary column head pressure and 24 kP_a secondary column head pressure at 40°C. A 1.0 s modulation period with a 0.07 duty cycle was used for all of the studies. The flame ionization detectors were maintained at a temperature of 340°C. Run times were approximately 35 min.

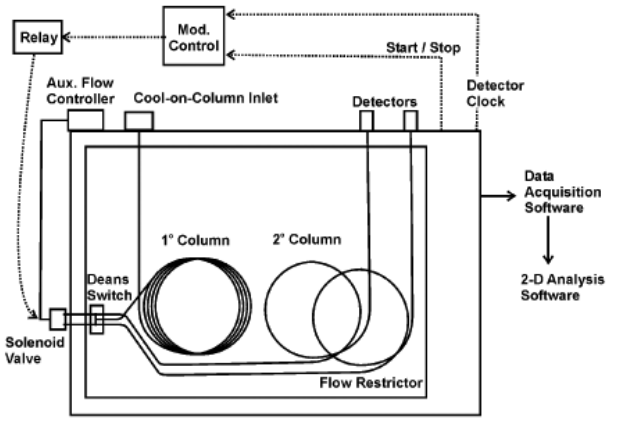

Figure 1. Schematic of the GC×GC instrument.

GC×GC analysis of fractionated fuels

A 1% mixture of diesel fuel in hexane was separated with a silica SPE cartridge into aliphatic and aromatic classes using a previously described methodology (EPA SW-846; Method 3630C). Briefly, the silica SPE column (20 mL, 5 g silica, Restek, pn# 26065) was washed with 10 mL methylene chloride followed by 20 mL hexanes. A 1 mL aliquot of a 1% diesel solution was then loaded. Aliphatics were eluted with 15 mL of hexanes in 5 mL increments. Aromatics were eluted with 20 mL of methylene chloride in 5 mL increments. All fractions were analyzed by GC×GC as described above. A 1% gas-oil sample in hexane (Supelco ASTM D2887 Reference Oil) was also analyzed in the same manner.

Calibration of the GC×GC instrument

Calibration was based on the analysis of aromatic/aliphatic reference standards containing 17 target polycyclic aromatic hydrocarbons (PAHs) and normal, aliphatic hydrocarbons, beginning with C_9 (*n*-nonane), including even-numbered hydrocarbons C_{10}–C_{30} and C_{36}. The list of standard compounds is shown in Table II. These hydrocarbons were dissolved in methylene chloride. Calibration curves and response factors were calculated for mixtures containing 1, 5, 10, 20, and 40 ppm of each individual compound.

Table I. GC×GC Experimental Conditions for Standards, Water, and Soil Sample Analysis.

Experimental Conditions	Standards and Water Sample Analysis	Soil Sample Analysis
Primary Column	DB-17HT (45 m × 0.25 mm × 0.15 µm)	ZB-50 (30 m × 0.25 mm × 0.25 µm)
Secondary Column	DB-1HT (2.5 m × 0.25 mm × 0.1 µm)	DB-1 (2.5 m × 0.25 mm × 0.1 µm)
Temperature Program	40°C for 3.25 min 13°C/min to 70°C 10.5°C/min to 120°C 9.5°C/min to 340°C hold at 340°C for 5 min	40°C for 2.5 min 12°C/min to 110°C 10.5°C/min to 340°C hold at 340°C for 5 min

Analysis of soil/wastewater samples with GC×GC

Soil and wastewater samples were extracted using methylene chloride (soils by sonication; waters by separatory funnel). The extract was dried over sodium sulfate and concentrated on a steam bath to a final volume of 1.0 mL. Concentrated extracts were treated with ~0.3 g loose silica gel to remove polar non-petroleum related compounds. These EPH extracts were then analyzed by GC×GC as previously described.

Soil/wastewater analysis with the conventional MA EPH method

Soil and wastewater samples were also analyzed with single-column GC–FID using the conventional MA EPH method for the purpose of comparison. Soil/wastewater samples were extracted with methylene chloride as described above for GC×GC analysis. The concentrated methylene chloride extract was solvent exchanged with hexane. The resulting hexane mixture was concentrated to a final volume of 1.0 mL and transferred to a 15-mL, 3-g disposable silica gel column for fractionation. The aliphatic components were first eluted off the silica gel by the addition of 1–2 mL aliquots of pentane. Each aliquot was allowed to elute by gravity through the column until a final volume of 10 mL of pentane had been collected. This was the aliphatic fraction. The elution procedure was repeated, using 1–2 mL aliquots of methylene chloride until 10 mL had been collected. This was the aromatic fraction. Each fraction was then concentrated to a final volume of 1.0 mL and analyzed by GC–FID. The GC–FID analysis entails the direct injection of 1.0 µL sample extract onto a Zebron ZB-5 30 m × 0.32 mm × 0.25 µm capillary column (Phenomenex). After a 2 min hold at 35°C, the GC oven was ramped at 10ºC/min to a final temperature of 310°C for a 6 min hold. The injector temperature was set at 300°C, and the FID temperature was set at 320°C.

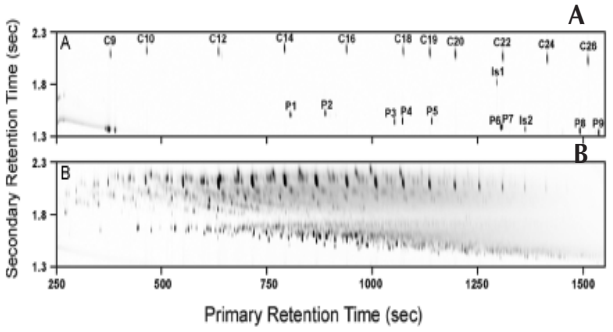

Figure 2. GC×GC chromatograms of a hydrocarbon standard mixture (A) and of 0.1% diesel fuel in methylene chloride (B). The peak labels in A correspond to the compounds listed in Table II.

Table II. Compounds Used for GC×GC Optimization and Calibration

Aliphatic Standard	Symbol	Aromatic Standard	Symbol
n-Nonane	C_9	Naphthalene	P1
n-Decane	C_{10}	2-Methylnaphthalene	P2
n-Dodecane	C_{12}	Acenaphthene	P3
n-Tetradecane	C_{14}	Acenaphthylene	P4
n-Hexadecane	C_{16}	Fluorene	P5
n-Octadecane	C_{18}	Phenanthrene	P6
n-Nonadecane	C_{19}	Anthracene	P7
n-Eicosane	C_{20}	Fluoranthene	P8
n-Docosane	C_{22}	Pyrene	P9
n-Tetracosane	C_{24}	Benz[a]anthracene	P10
n-Hexacosane	C_{26}	Chrysene	P11
n-Octacosane	C_{28}	Benzo[k]fluoranthene	P12
n-Triacontane	C_{30}	Benzo[b]fluoranthene	P13
n-Hexatriacontane	C_{36}	Benzo[a]pyrene	P14
Internal Standard		Dibenz[a,h]anthracene	P15
1-Chlorooctadecane	Is1	Indeno[1,2,3-cd]pyrene	P16
o-Terphenyl	Is2	Benzo[ghi]perylene	P17

Results and Discussion

Optimization of the GC×GC Separation

The GC×GC experimental conditions were optimized by analyzing a standard sample containing C_9–C_{36} straight chain aliphatics and 17 PAHs. The compounds are listed in Table II. A portion of a typical chromatogram is shown in Figure 2A. The widths at half maximum of the peaks along the primary dimension were 2 s. The alkanes displayed high secondary retention and the PAHs had low secondary retention. This secondary retention order was produced by employing an intermediate polarity primary column and a non-polar secondary column. The widths at half maximum of the PAH peaks were approximately 40 ms along the secondary dimension, while those of the alkanes were approximately 70 ms.

Highly symmetric peaks with no tailing were observed when the apparatus was initially assembled. However, after several weeks of operating at temperatures as high as 340°C, peak tailing along the secondary dimension was observed. High temperatures are believed to have played a significant role in producing the tailing, as this condition was never observed when the Dean's switch was used for more than 1 year at temperatures less than 300°C (21). The greatest amount of tailing was observed for the large alkanes and large PAHs. The exact source of the tailing is unknown; however, it was narrowed down to somewhere within the Dean's switch modulator, as installing new columns did not change the condition. In addition, a small loss (approximately 20%) in the efficiency of transfer of components from the primary column to the secondary column was observed at low concentrations (< 5 ppm) for low-volatility compounds. This observation can be explained by assuming that some hydrocarbon is temporarily adsorbed to the internal surfaces of the Dean's switch, and does not reach the secondary column during the 0.07 s injection portion of the modulation cycle. It is possible that this problem would be alleviated with a better inert coating on the internal surfaces of the Dean's switch or by placing the Dean's switch in a heated enclosure.

Analysis of petrochemical samples

Dilute mixtures of petrochemical samples were analyzed by GC×GC. Figure 2B shows a 0.1% diesel fuel in methylene chloride. The upper portion of the chromatogram contains aliphatic compounds, while the lower portion of the chromatogram is occupied by aromatic compounds. These two regions are fully resolved in the secondary dimension for primary retention times up to 850 s (approximately where C_{14} elutes). At retention times greater than 850 s, the aromatic and aliphatic regions converge. However, a distinct "signal valley" is always present between the two regions. Fortunately, this valley has a much lower signal intensity than the maximum intensities of the surrounding

aliphatic or aromatic regions: The major aliphatic components had peak heights approximately 200 pA above baseline, while the major aromatic components had peak height approximately 100 pA above baseline. In contrast, the "signal valley" was only 4 pA above baseline. Petrochemical mixtures containing higher boiling compounds than diesel fuel, such as gas-oil, were also analyzed with similar results.

GC×GC analysis of aromatic and aliphatic fractions isolated with SPE

SPE fractionation of diesel fuel was performed to characterize the extent of overlap between the aliphatic and aromatic regions. A 1 mL quantity of 1% diesel fuel in hexanes was loaded onto a silica SPE cartridge. A total of 15 mL of hexanes was used to elute the aliphatic hydrocarbons in 5 mL increments. A total of 20 mL of methylene chloride was used to elute the aromatic hydrocarbons in 5 mL increments. GC×GC analysis was performed on each 5 mL fraction. The chromatograms that displayed significant levels of hydrocarbon are shown in Figure 3, along with a chromatogram of unfractionated 0.2% diesel fuel.

For each chromatogram, a horizontal dotted line was drawn at a secondary retention time of 1.7 s. This line represents the location of the signal minimum separating the two compound classes. The fractionated data show that greater than 97% of the peak area due to the aliphatic compounds was above the dotted line, and greater than 95% of the peak area due to the aromatic compounds was below the dotted line. This indicates that overlap of these regions is minimal.

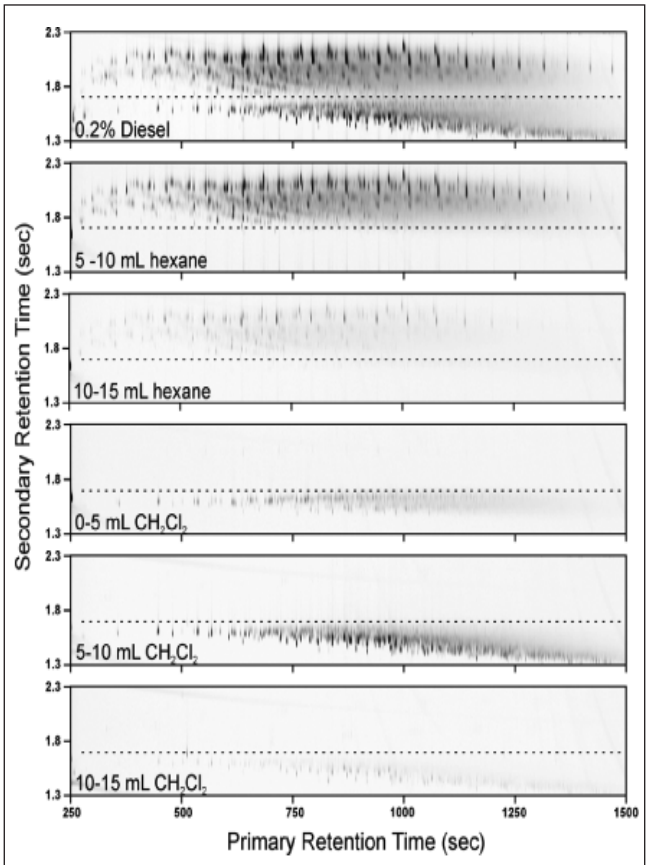

Figure 3. GC×GC chromatograms of 0.2% diesel fuel in hexane and individual fractions resulting from a SPE separation of a diesel fuel sample. The dotted line represents the assigned border between the aliphatic and aromatic region of the chromatogram. Aliphatic peaks are located above the border, while aromatic peaks are located beneath the border.

The limited overlap of the aromatic and aliphatic regions of the GC×GC chromatograms suggest that these classes can be accurately quantified by GC×GC without prior fractionation. To test this assertion, the unfractionated diesel fuel chromatogram was analyzed by assigning all of the peak area above the 1.7 s border to the aliphatic class and assigning all of the peak area below the border to the aromatic class. With this approach, 67% of the total peak area was assigned to the aliphatic class, while the remaining 33% was assigned to the aromatic class. The fractionated chromatograms were analyzed without this assumption, as only aliphatics were present in the three hexane fractions and only aromatics were present in the methylene chloride fractions. The total peak area of the hexane fractions was 66% of the total peak area of all of the fractions. The total peak area of the methylene chloride fractions was 34% of all of the fractions. The class distribution found with direct GC×GC analysis of unfractionated fuel is in excellent agreement with the results obtained from analysis of the fractionated samples. This result provides preliminary evidence that accurate GC×GC analysis of petroleum-contaminated water and soil can be conducted without the need for prior SPE fractionation.

Calibration of the GC×GC method

Five standard mixtures were analyzed. The mixtures contained each of the 14 aliphatic compounds and 17 PAHs at concentrations of 1, 5, 10, 20, or 40 ppm. The hydrocarbons were dissolved in methylene chloride. Each mixture was analyzed twice. The individual peak areas determined in these two analyses agreed to within 3% for the majority of the compounds; however, the large PAHs had deviations near 10%. Plots of peak area as a function of compound concentration resulted in strong linear correlations for each component: the R^2 values of the linear fits were generally greater than 0.9995. A slight negative intercept was observed for most components. This was most likely due to the decrease in the primary to secondary column transfer efficiency that was observed for compounds at low concentration. Response factors (i.e., peak area/component concentration) were calculated for each component at each concentration. The average response factors, along with relative standard deviations, (RSDs) were calculated for each individual component. The RSDs of the response factors were approximately 7%.

Analysis of water samples

Water samples were prepared for GC×GC analysis using a method that employs the first three steps of the MA EPH method, followed by a clean-up step. Water samples (1000 mL) were first extracted with methylene chloride, dried with sodium sulfate, and concentrated by evaporation down to a volume of 1.0 mL. The concentrated samples were then treated with 0.3 g of loose silica gel to remove compounds more polar than PAHs (e.g., alcohols, carboxylic acids, etc.). The resulting mixtures were analyzed by GC×GC.

Spiked water samples

Two 1.0 L volumes of deionized water were independently spiked with 40 ppb of each of the aliphatic and PAH hydrocarbons (see Table II). These spiked water samples were put through the sample preparation procedure. The resulting extracts were individually analyzed four times over a period of two weeks. A significant difference between the two water samples was not observed. The average RSDs of the peak areas of the individual components were approximately 8%, with lower RSDs observed for the smaller compounds and higher RSDs observed for the larger compounds.

The response factors determined from the analysis of the calibration mixtures (see the previous section) were used to calculate the concentration of each hydrocarbon in the original water samples. The measured concentrations for the more volatile alkanes (C_9 to C_{12}) were approximately 25% lower than the original 40 ppb spiked level. Nonane (C_9) had the lowest value. The negative deviation is most likely due to evaporative loss during the sample concentration step. A similar loss was observed with the conventional MA EPH method. The measured concentrations for alkanes of moderate size (C_{14} to C_{24}) were within 5% of 40 ppb. The measured concentrations for the large alkanes (C_{26} to C_{36}) were approximately 30% lower than the spiked levels, with C_{36} having the lowest value. This negative deviation could be derived from multiple sources: (*i*) loss of alkanes during sample preparation; (*ii*) decrease in modulator transfer efficiency observed for large compounds; and/or (*iii*) loss of larger alkanes in the injection port. The measured concentrations of the first 14 PAHs were all within 10% of the 40 ppb values, while the last three PAHs (P15–P17) were 20% higher than the spiked levels.

The MA EPH method quantifies the levels of the hydrocarbons in 3 different compound classes: aliphatics eluting from C_9 to C_{18}, aliphatics eluting from C_{19} to C_{36}, and aromatics eluting from naphthalene to benzo[ghi]perylene. The average response factors and total peak areas for the members of these groups were combined to generate a measurement of the total amount of hydrocarbon in each of these classes. The C_9–C_{18} aliphatic class had a measured concentration of 202 ppb compared to a spiked level of 240 ppb (16% low). The C_{19}–C_{36} aliphatic class had a measured concentration of 273 ppb compared to a spiked level of 320 ppb (14% low). Finally, the aromatics had a measured concentration of 681 ppb compared to a spiked concentration of 680 ppb.

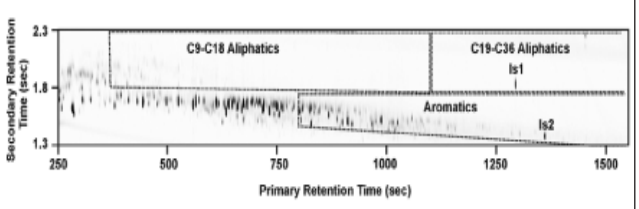

Figure 4. GC×GC chromatogram of an extracted wastewater sample. The regions of the chromatogram assigned to the C_9–C_{18} aliphatic class, C_{19}–C_{36} aliphatic class, and naphthalene to belzo[ghi]perylene class are shown. The identities of the internal standard peaks are listed in Table II. The areas of the internal standard peaks were not included in the total areas of the hydrocarbon regions.

These analyses show that the GC×GC method in its current form does produce quantitative results with statistically significant deviations from the actual values. However, it is important to note that these deviations fall well within those frequently observed using the conventional MA EPH method. The MA EPH method considers quantitative results within 40% to 140% of the actual value to be acceptable (1). Thus, the GC×GC analysis without prior fractionation generates results that are acceptable by the conventional standards.

Wastewater samples

Four different wastewater samples were analyzed with the GC×GC method and with the conventional MA EPH method. A GC×GC chromatogram of a typical water sample is shown in Figure 4. Numerous well-resolved peaks were observed in the aromatic region of the chromatogram. Unfortunately, many of these peaks fell beneath the region occupied by aromatic hydrocarbons. This indicates that compounds other than petroleum hydrocarbons were in the analyzed extracts. Thus, the sample clean-up step employing loose silica gel was insufficient to completely remove all of the polar, non-petroleum compounds. The samples were still analyzed for petroleum content under the assumption that all peaks falling within the chromatographic regions occupied by petroleum hydrocarbons were in fact hydrocarbons and not non-petroleum compounds. The chromatographic regions that were assigned to the C_9–C_{18} aliphatic class, C_{19}–C_{36} aliphatic class, and naphthalene-benzo[ghi]perylene class are shown in Figure 4. The concentrations of the hydrocarbons in the water samples were calculated using the average response factors for each group and the relevant dilution factors.

The compiled results for the four wastewater samples are shown in Table III, along with a comparison to the values obtained with the conventional MA EPH method. A clear trend is present in the data: (*i*) The aromatic levels determined by the GC×GC method are higher than those observed by MA EPH. (*ii*) The aliphatic levels determined by the GC×GC method are lower than those determined by the MA EPH method. It is most likely that several factors create these discrepancies. It should be noted that the magnitude of the observed discrepancies are larger than deviations caused by adsorption in the modulator. It is also highly unlikely that aliphatic hydrocarbons were improperly assigned to the aromatic class in the GC×GC chromatograms due to overlap of the aliphatic and aromatic regions. This is because the aliphatic hydrocarbons observed in these samples were much smaller than the size where the aliphatic and aromatic regions start to converge (i.e., the aliphatics were smaller than C_{14}).

The first possible cause for the high GC×GC values for aromatics is that non-petroleum compounds were present in the region of the chromatogram assigned to the aromatics. Such a deviation is caused by insufficient sample clean-up prior to analysis. The second possible cause of high GC×GC aromatic values and low GC×GC aliphatic values is that the MA EPH analyses were actually in error: It is possible that a substantial breakthrough of aromatic compounds into the aliphatic fraction occurred during the SPE fractionation step of the MA EPH method. Such an error would lead to the MA EPH aliphatic values being erroneously high, the aromatics erroneously low,

and the total hydrocarbon values being essentially accurate. This source of error is most consistent with the data: all of the MA EPH aliphatic values are higher than the corresponding GC×GC values; all of the MA EPH aromatic values are lower than the corresponding GC×GC values; and the total hydrocarbon levels determined by the MA EPH method samples #2, #3, and #4 all agree with their corresponding GC×GC values to within 21%. Independent analysis of the fractionated water extracts with both the MA EPH method and the GC×GC method would be beneficial for determining the source of this discrepancy. Such experiments are planned for the future.

Analysis of soil samples

Soil extracts were prepared using the same drying, concentration, and clean-up procedure used for the GC×GC analysis of water samples. A chromatogram of a typical soil extract is shown in Figure 5. A chromatogram of the standard mixture containing the target PAHs and aliphatics is also shown at the top of Figure 5. The GC×GC chromatograms of soil had very small aliphatic peaks. The vast majority of the peaks were located in a band at the base of the chromatogram. This band is occupied by PAHs. Comparison of the chromatograms shown in Figure 5 shows that the largest peaks in the soil sample correspond to the target PAHs. This is not surprising, as the soils were known to be contaminated with creosote. Creosote contains all target PAH compounds, with a relatively significant concentration of the later-eluting PAHs, as well as aromatic constituents of the black, amorphous residue of coal tar pitch.

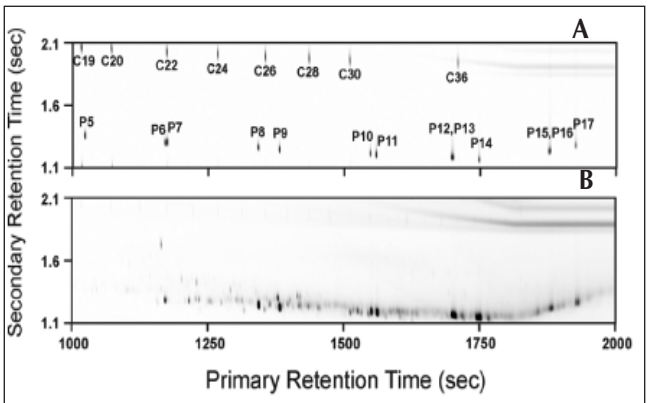

Figure 5. GC×GC chromatograms of a hydrocarbon standard (A) and of an extracted soil sample (B). The identities of the labeled peaks in A can be found in Table II. The soil chromatogram shows low levels of aliphatics but high levels of many of the PAHs found in the standard mixture.

In general, the GC×GC method observed lower levels of alkanes and higher levels of aromatics. The agreement between the aromatic values is better for the soil analyses than the water analyses. The sources of error described for the water analyses also apply to the soil analyses. In addition, there are sources of variance that are unique to the soil analyses. For example, the samples are not homogenized prior to analysis, as per the MA EPH method (1), in order to maintain the volatile content and integrity of the sample. This can result in "hot spots" within the soil where there is a region of heightened analyte concentration.

Conclusions

A flow-switching GC×GC method has been created for separating complex hydrocarbon mixtures such as diesel fuel, gas-oil, and the extracts of petroleum-contaminated samples. The GC×GC system generates two-dimensional chromatograms with minimal overlap between the aliphatic and aromatic regions. These regions can be separately integrated to provide accurate and essentially independent quantitation of aliphatics and aromatics without prior fractionation. Van De Weghe et al. made a similar conclusion for thermal modulation GC×GC (23).

The flow-switching GC×GC system can operate at temperatures as high as 340°C. However, peak tailing along the secondary dimension was observed after extended use at elevated temperatures. The exact source of the tailing is unknown, but the concurrent loss in the efficiency of transport of components from the primary column to the secondary column indicates that components are temporarily adsorbed onto the internal surfaces of the Dean's switch modulator. Future work will test the use of different internal coatings and placing the Dean's switch in a heated enclosure.

The GC×GC system was used to analyze extracts of spiked water samples, wastewater, and soil. The accuracy of the method was compared to that of the Massachusetts method for analyzing extractable petroleum hydrocarbons. The GC×GC system generated a quantitative accuracy for the analysis of spiked water that was well within the MA EPH criterion of acceptability (1). The GC×GC method and the MA EPH method generated comparable levels of total hydrocarbons when

Table III. Summary of Wastewater Analyses

	GC×GC Concentrations (ppb)			MA EPH Concentrations (ppb)		
Sample	C_9–C_{18}	C_{19}–C_{36}	Aromatic	C_9–C_{18}	C_{19}–C_{36}	Aromatic
Water #1	40.9	ND	671	100	ND	350
Water #2	34.9	ND	526	260	ND	220
Water #3	50.2	ND	1076	1200	ND	210
Water #4	58.2	ND	624	380	ND	300

Table IV. Summary of Soil Analyses

	GC×GC Concentrations (ppm)			MA EPH Concentrations (ppm)		
Sample	C_9–C_{18}	C_{19}–C_{36}	Aromatic	C_9–C_{18}	C_{19}–C_{36}	Aromatic
Soil #1	2.1	19.2	629	22	49	260
Soil #2	0.4	9.6	561	3.2	10	295
Soil #3	ND	ND	850	19	115	677
Soil #4	6.1	19.4	733	103	314	826

wastewater was analyzed, but the GC×GC method detected a significantly higher aromatic content and lower aliphatic content. This could be caused by incomplete clean-up of non-petroleum related compounds prior to GC×GC analysis. Future work will focus on evaluating the effectiveness of the quick silica clean-up step employed in the current GC×GC sample preparation method. It is also possible that the GC×GC method detected higher aromatic levels and lower aliphatic levels because the MA EPH results were in error. The observed discrepancy would occur if aromatics broke through into the aliphatic fraction during the MA EPH fractionation step. Both the GC×GC method and MA EPH method measured comparable levels of aromatics in the soil samples.

Acknowledgements

This research was supported, in part, by the National Science Foundation grant number 0094185. The authors would like to thank Agilent Technologies, Inc., for lending the 6890N gas chromatograph and many of the consumables used for this study.

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Manuscript received April 30, 2007;
revision received July 31, 2007.