Comprehensive Two-Dimensional Gas Chromatography for Fast Screening of Wash Oils

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Abstract

Fast screening of wash oils is demonstrated using comprehensive two-dimensional gas chromatography (GC×GC). Wash oils are used in ethylene production plants to minimize compressor fouling. The composition of a wash oil determines its effectiveness in solubilizing heavy hydrocarbons. In particular, the relative amount of 1- and 2-ring aromatics is important. The presence of oxygenates is undesirable because of adverse effects to the process. It is shown that GC×GC is well suited for this application. Species in wash oils are separated and grouped into three bands: a nonpolar aliphatics band, 1- and 2-ring aromatics band, and polyaromatics band. For a given polar secondary column, the spacing between bands in the second dimension can be adjusted in a broad range by selecting a primary column and an oven-temperature-programming rate. Integration of GC×GC peaks is evaluated using a standard GC integration program and a new GC×GC integration program. Consistent results are obtained using both programs for well-separated GC×GC peaks with relative differences for individual peak ranging from 0.04% to 1.6%. Peak responses are integrated by the GC×GC software, and the relative amounts of aromatics content and aliphatics content are estimated by peak response percent with relative standard deviations ranging from 0.15% to 2.8% (n = 3).

Introduction

In ethylene production plants, cracked gas compressors experience fouling on the wheels (rotors) and diaphragms. This is more of a problem in ethylene plants that use light feedstock. When the compressor fouls, the efficiency decreases, requiring more horsepower to do the same amount of compression. Vibration may be induced because of the imposed imbalance on the wheels.

Compressor fouling can be controlled primarily through use of liquid hydrocarbon wash oils (1). Wash oil has four functions. First, the wash oil physically rinses away fouling matter by removing it from the cracked gas compressor. Second, it dissolves fouling deposits before they can be fully dehydrogenated. Third, the wash oil wets the surfaces of the wheels and diaphragms and prevent sticking of tars and polymers. Finally, if used continuously, wash oil has the ability to cool process gases by partial vaporization of itself.

A good wash oil should have good solvency characteristics, which usually means high aromatics content. It should also have a high mid-range boiling point. It should have low solids and gums content. It is important that the wash oil contains little or no water-soluble components. The presence of oxygenates is undesirable because oxygenates will make waste water treatment more difficult.

Comprehensive two-dimensional gas chromatography (GC×GC) was developed by Phillips and Liu in 1991 (2). In a GC×GC system, the effluent eluted from the primary column is focused and reinjected into the secondary column through a modulator to complete a two-dimensional separation process every several seconds. It is different from the heart-cut two-dimensional GC in which only a fraction of the sample will go through the two-dimensional separation process; the GC×GC technique applies the two-dimensional separation process to the entire sample, typically, in 1–15-s increments. Generally, a long nonpolar column is used as the primary column, a short narrow-bore polar column is used as the secondary column, and the compounds are grouped into different bands by their chemical properties. Several articles have been published to review the modulation technologies and discuss basic concepts of GC×GC (3–9). In the last ten years, approximately 100 GC×GC papers have been published for a broad range of GC×GC applications, including pesticides (10), polychlorinated biphenyls (11), gasoline (12), petroleum (13,14), and essential oils (15). Recently, a monograph authored by Blomberg has described the characterization of petrochemicals by GC×GC and other multidimensional technologies (16).

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GC×GC was used to characterize wash oils for fast screening and quantitating total 1- and 2-ring aromatics content in this paper. To monitor oxygenates, a wax column was used as the secondary column to achieve a good separation between oxygenates and hydrocarbons in wash oils. Aliphatic compounds, 1- and 2-ring aromatic compounds, and polyaromatic compounds in wash oils can be grouped into different bands by GC×GC. The aromatics content was estimated by response percent of GC×GC peaks.

Experimental

GC×GC modulator

An HP 6890 GC (Agilent Technologies, Wilmington, DE) equipped with an flame ionization detector and a split/splitless injector was used. A Zoex loop modulator (Zoex Corp., Lincoln, NE) was mounted onto the HP 6890 GC. A schematic diagram of the loop modulator and timing cycle of the hot jet valve are shown in Figure 1. The modulator consisted of a cold nitrogen gas jet, pulsed hot nitrogen gas jet, and trapping loop. A piece of uncoated fused-silica capillary column (100-cm × 100-µm i.d.) was used for the trapping loop. Nitrogen gas from a compressed gas cylinder was cooled using a heat exchanger immerged in a liquid nitrogen dewar to provide the cold jet gas. The cold jet remained on throughout the analysis to form two cold trapping zones in the loop: the first and second trap stages. Effluents from the primary column were trapped and compressed into sharp bands in the trapping zones. When the pulsed hot jet opened for a short period of time, solutes trapped in the second stage were instantly remobilized to the secondary column; the solutes released from the first stage were trapped again in the second stage. The modulation cycle then repeated itself for the entire sample.

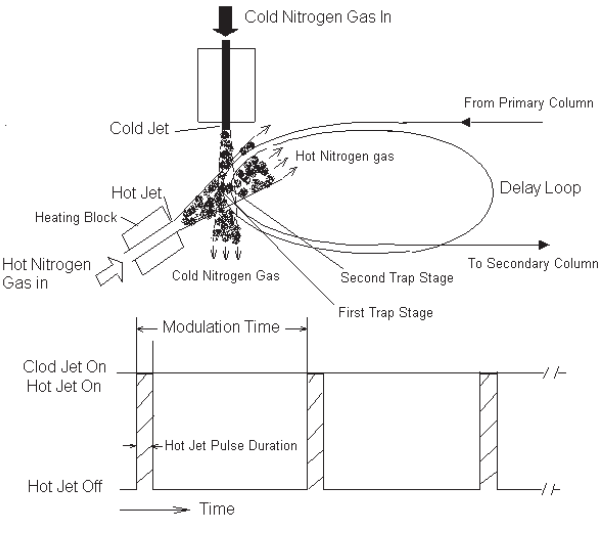

Figure 1. Schematic diagram of Zoex loop modulator (top) and timing cycle of hot air jet valve (bottom).

Column set and separation conditions

Column set and GC×GC conditions 1

A nonpolar DB-5 column (15-m × 0.25-mm i.d., 1.0-µm film thickness) (Agilent Technologies) was used as the primary column, and a short narrow-bore polar DB-Wax column (90-cm × 100-µm i.d., 0.1-µm film thickness) was used as the secondary column. The two columns were connected to the two ends of the modulation loop using GC Press-Tight connectors (Restek, Bellefonte, PA). Both columns were installed in the same oven. Helium was used as the carrier gas, and a constant pressure of 18 psig was used for the analysis. The oven temperature was held at 50°C for 1 min, then ramped at 5°C/min to 250°C, and held for 29 min. The temperature of the split injector was 250°C, and the split flow rate was set to 30 mL/min. The detector temperature was 350°C. Two wash oils (wash oils A and B) were analyzed. One-microliter aliquots of wash oils were injected using an automatic sampler. A modulation time of 5 s and a hot N_2 pulse duration of 250 ms were used for the analysis. The pulse duration should not be too long, otherwise breakthrough in the trapping loop occurs, and solutes released from the first stage pass through the second stage before the pulsed hot jet shuts off.

Column set and GC×GC conditions 2

A nonpolar DB-1 column (15-m × 0.25-mm i.d., 0.25-µm

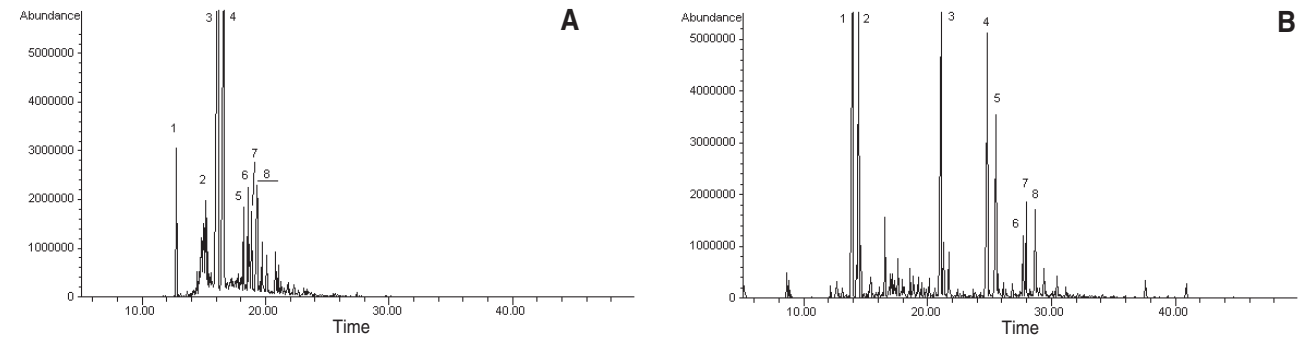

Figure 2. (A) Total-ion chromatogram of wash oil A: triethylbenzene (1), (2) triethylbenzene, (3) diphenylethane, (4) 1,1'-ethylidene bis[4-methylbenzene], (5) isomer of 4, (6) 1,1-bis[p-ethylphenyl] ethane, (7) isomer of 6, and (8) isomers of 6. (B) Total-ion chromatogram of wash oil B: (1) naphthalene, (2) dihydromethyl-naphthalenes, (3) isomer of methyl-naphthalene, (4) isomer of methyl-naphthalene, (5) biphenyl, (6) isomer of ethyl-naphthalene, (7) isomer of ethyl-naphthalene, and (8) dimethyl-naphthalenes.

film thickness) was used as the primary column, and a short narrow-bore polar DB-Wax column (100-cm × 100-µm i.d., 0.-µm film thickness) was used as the secondary column. Helium was used as the carrier gas, and a constant flow rate of 1.2 mL/min (41.1 psig at 80°C) was used for the analysis. The oven temperature was held at 80°C for 1 min, then ramped at 2°C/min to 250°C, and held for 0 min. The temperature of the split injector was 250°C, and the split flow rate was set to 50 mL/min. One-tenth-microliter aliquots of wash oils were injected using an automatic sampler. A modulation time of 16 s and a pulse duration of 250 ms were used for the analysis.

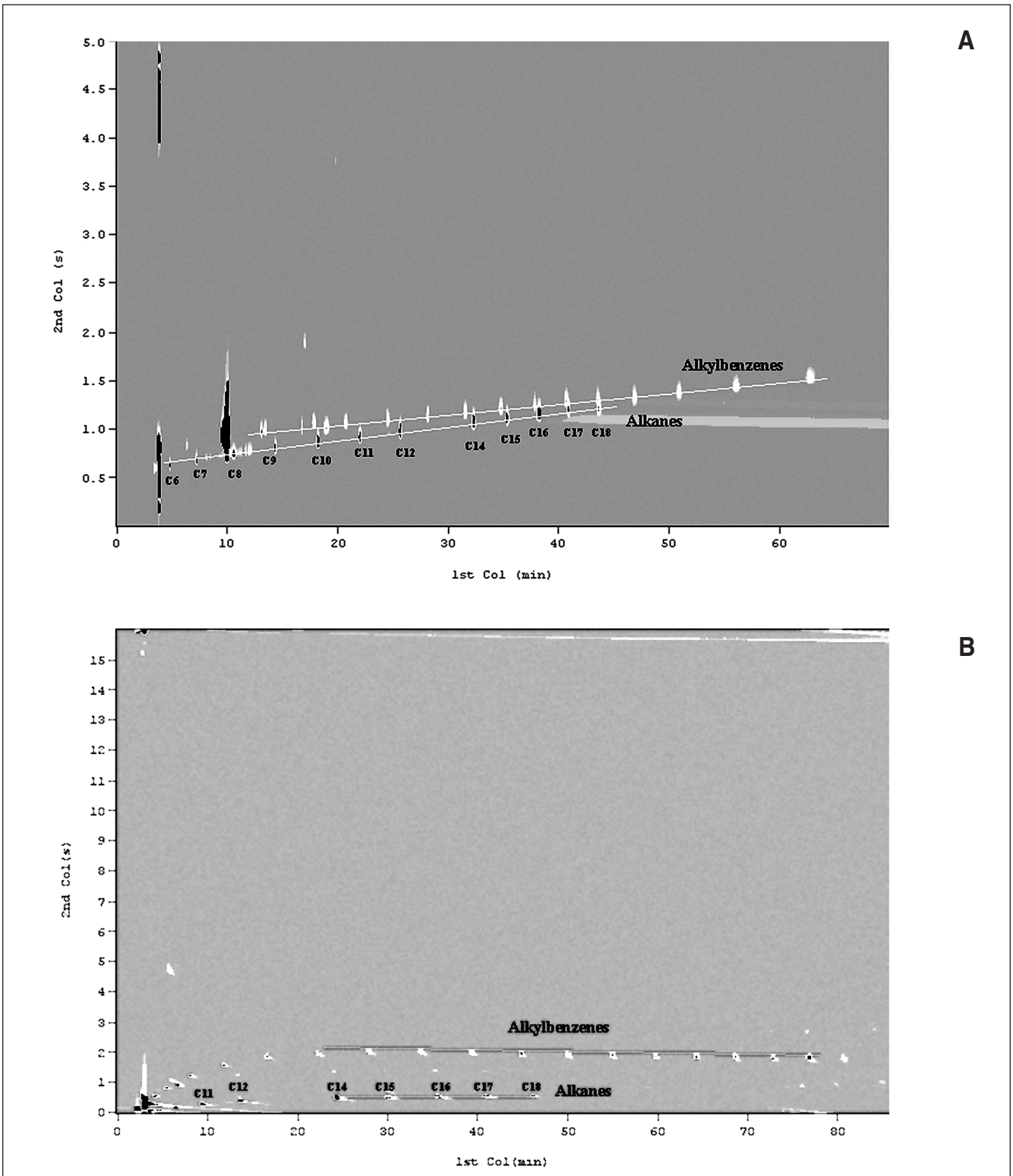

Figure 3. Contour plots of alkanes and alkylbenzenes using column set and conditions 1 (A) and column set and conditions 2 (B).

Data collection and processing

All GC data were collected by Agilent ChemStation at a sampling rate of 100 Hz. The raw GC data were exported from ChemStation to a file in comma-separated values format and were later processed by the GC×GC software. Integration of the GC×GC data was performed using GC Image prerelease edition (August 2002, University of Nebraska–Lincoln, Lincoln, NE). Because the current model of Zoex thermal modulator does not synchronize the start of GC and the start of the modulation process, the phase shift was performed by the software on each contour plot to move it to the same position. This process makes it difficult to obtain correct retention times on the sec-

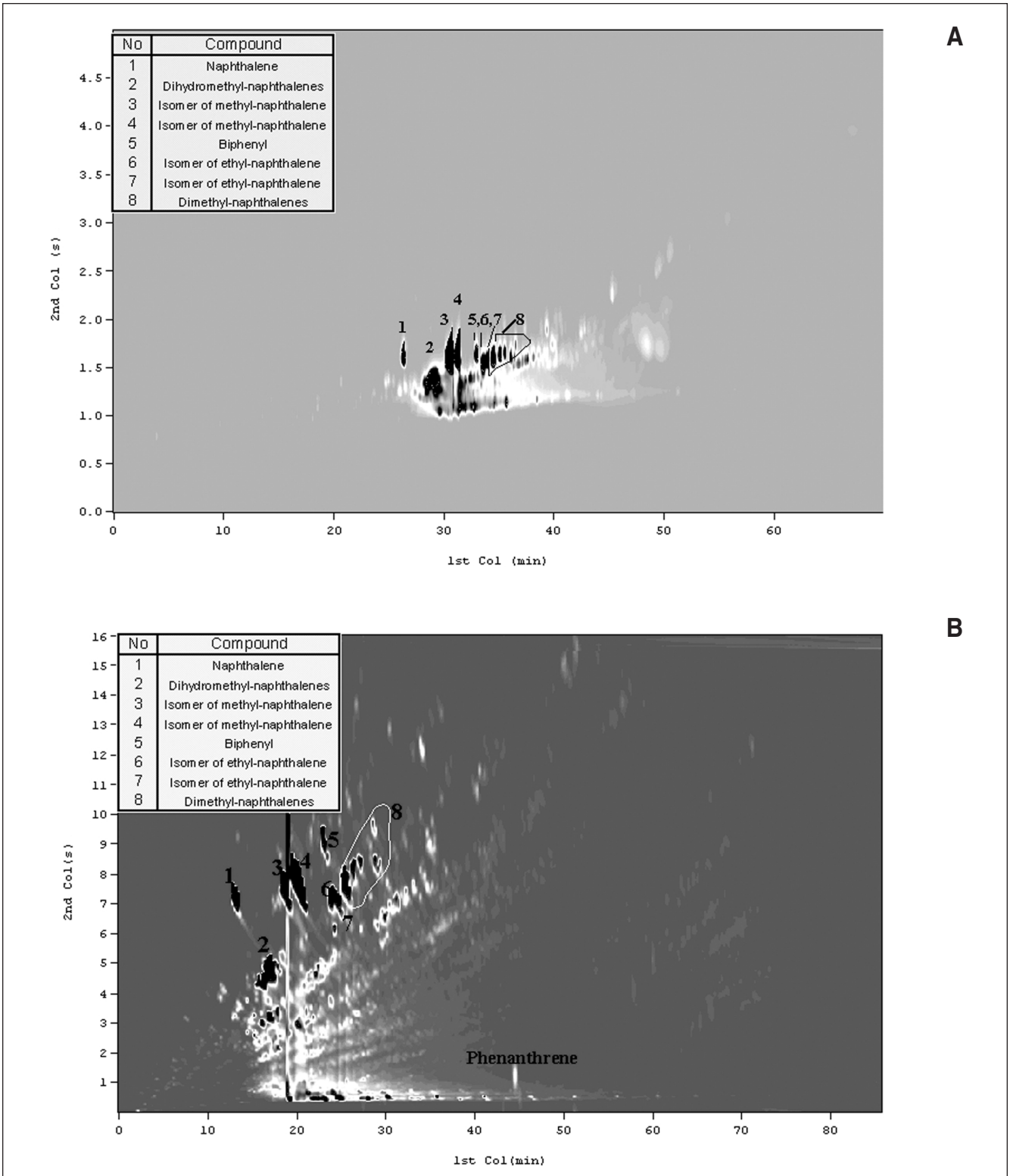

Figure 4. Contour plots of wash oil A using column set and conditions 1 (A) and column set and conditions 2 (B).

ondary dimension. Recently, Zoex has provided an upgrade of the pulser generator, which will synchronize the start of GC and the start of the modulation process.

GC–mass spectrometry and GC–atomic emission detection

The major components were identified by GC–mass spectrometry (MS) using an HP-5 MS column (30-m × 0.25-mm i.d., 0.25-µm film thickness) and Agilent 5973 mass selective detector. The samples were also analyzed by GC–atomic emission detection (AED) to determine if oxygenates were present in the wash oils. An HP-5 column (30-m × 0.32-mm i.d., 0.32-µm film thickness) and an Agilent G2350A AED were used to

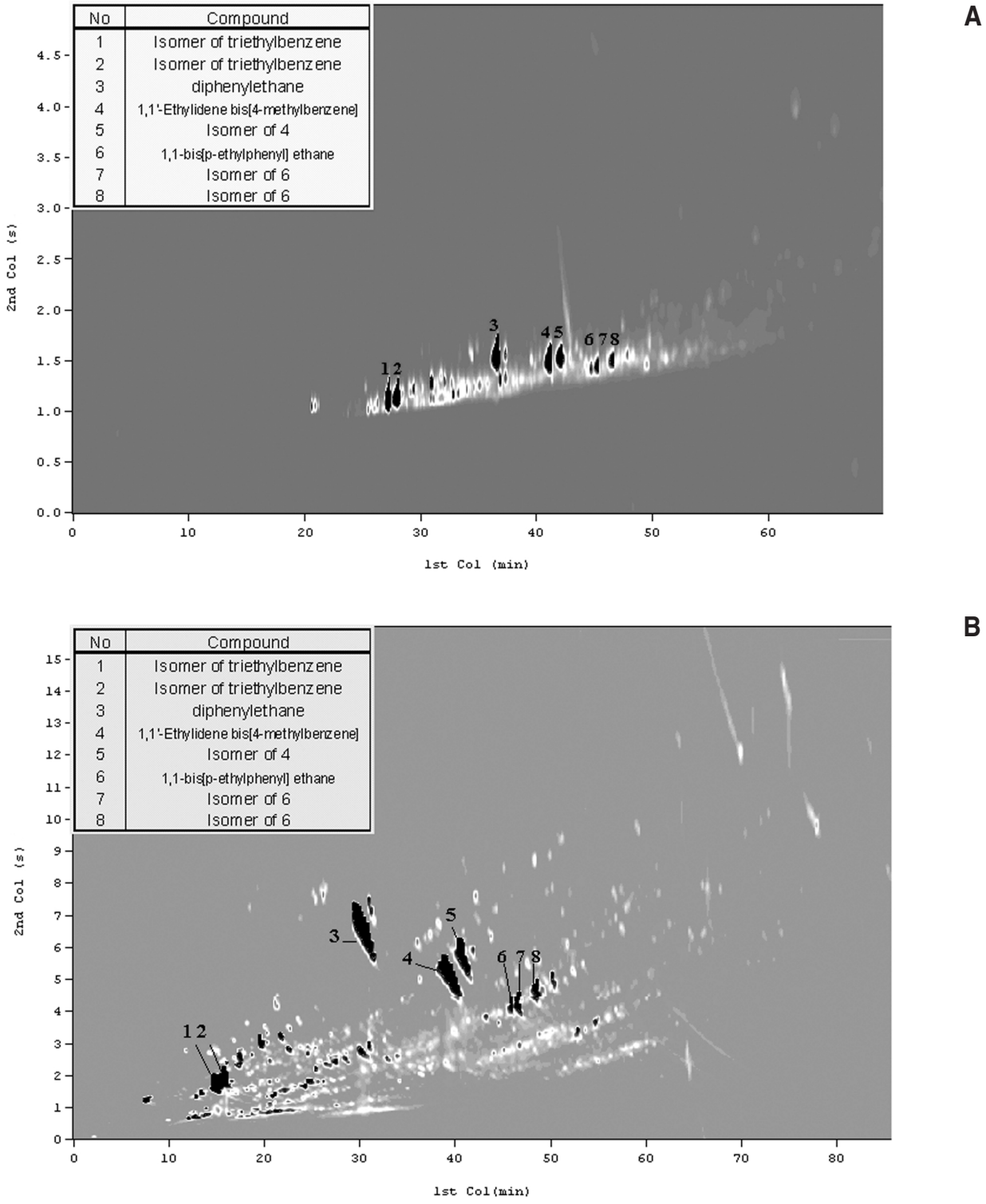

Figure 5. (A) Contour plots of wash oil B using column set and conditions 1 (A) and column set and conditions 2 (B).

Peak Identifications:

A = Styrene GC×GC peaks

B = Cumene GC×GC peaks

C = Naphthalene GC×GC peaks

D = Biphenyl GC×GC peaks

E = Phenanthrene GC×GC peaks

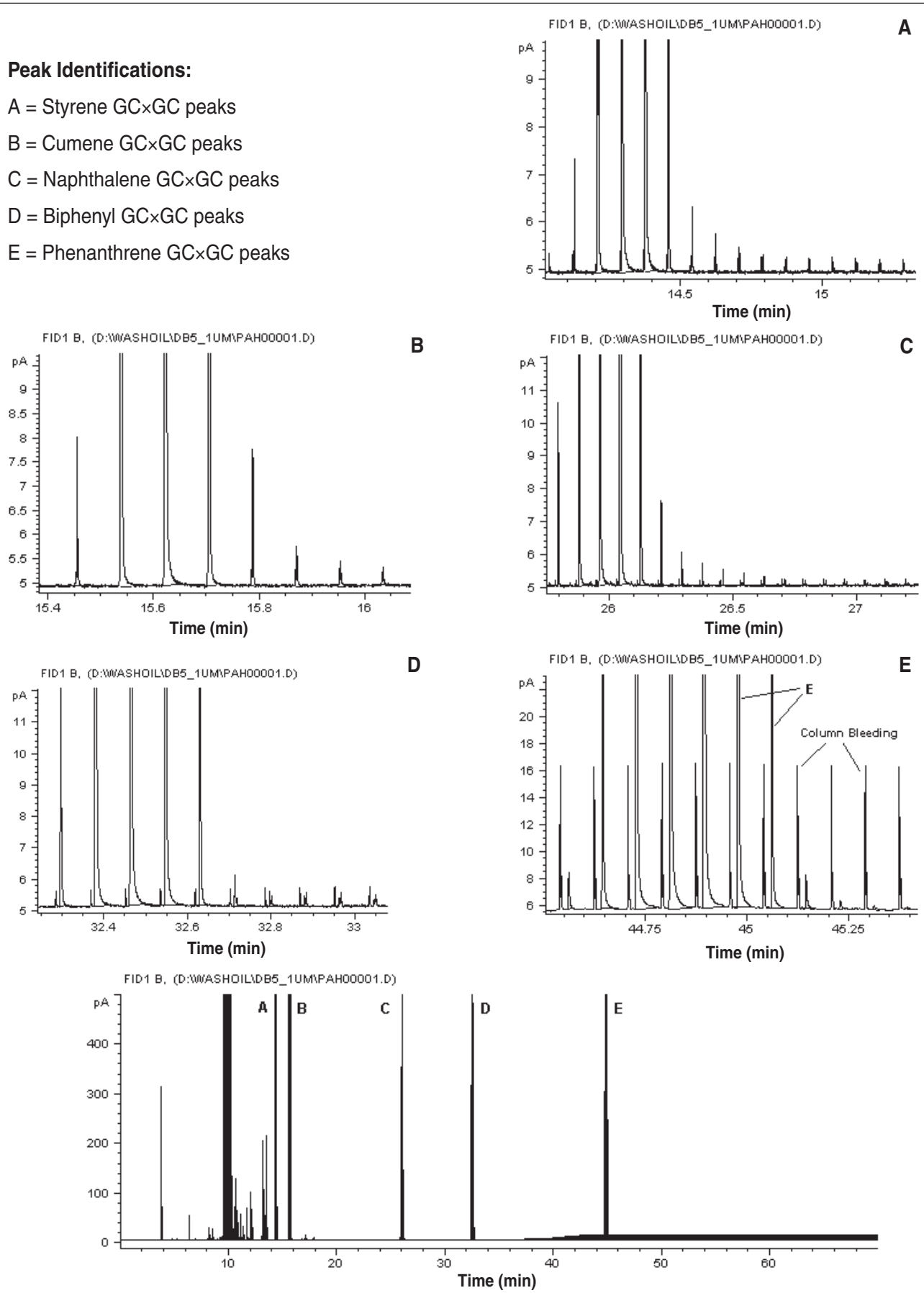

Figure 6. Integration of modulated GC×GC peaks by Agilent ChemStation using column set and conditions 1.

selectively detect carbon-containing compounds at 179 nm, sulfur-containing compounds at 181 nm, nitrogen-containing compounds at 174 nm, and oxygen-containing compounds at 171 nm.

Results and Discussion

GC×GC separations

Good wash oils contain a high level of aromatic compounds (1). A GC–MS system could be used to characterize the wash oil by identifying individual components. Figures 2A and 2B show total-ion chromatograms of wash oils A and B. They are complex mixtures with large numbers of coeluting peaks. It would be difficult to quantitate aliphatics and aromatics content based on the single dimension chromatograms.

Alternatively, a GC×GC system can facilitate the characterization process by grouping components into different bands according to their chemical properties. Schoenmakers et al. discussed the comparison of GC×GC and GC–MS to characterize complex hydrocarbon mixtures (17). In general, the GC×GC system was shown to be a powerful tool for group analysis by separating components into different bands. Beens and Blomberg discussed how to tune a GC×GC system for oil samples by using different columns (16,18). For wash oils, an intermediate polar column, like SGE BPX-50 (50% phenyl, SGE International Pty Ltd., Victoria, Australia), is appropriate for the secondary column. However, wax columns generally provide better resolution for oxygenates and were used as the secondary column for wash oils to observe the possible presence of oxygenates. The selectivity of the secondary column plays a key role in overall GC×GC separation. After the secondary column is selected, the GC×GC system can also be adjusted to achieve different resolution in the secondary dimension by choosing a primary column and an oven temperature-programming rate. A second oven independently controlled for the secondary column can also be used to further enhance overall resolution and tuneability. Ong et al. reported extensive studies on effects of column temperature program rate, column flow rate, sta-

Table I. Comparison of Integration Results Using GC Image and ChemStation

		GC×GC software: GC Image		Agilent Chemstation		
Peak no.	Names	Response	Response%	Area	Area%	Difference%*
1	Styrene	216924.33	60.43	2168.96	60.53	–0.2
2	Cumene	40646.76	11.32	405.96	11.33	–0.1
3	Naphthalene	49920.66	13.91	498.90	13.92	–0.1
4	Biphenyl	21729.08	6.053	216.81	6.051	0.04
5	Phenanthrene	29770.98	8.293	292.57	8.165	1.6
Total		358991.81	100.0	3583.19	100.0	

* Difference percent is calculated by the equation: [(response % by GC Image – response % by ChemStation/response % by ChemStation] × 100.

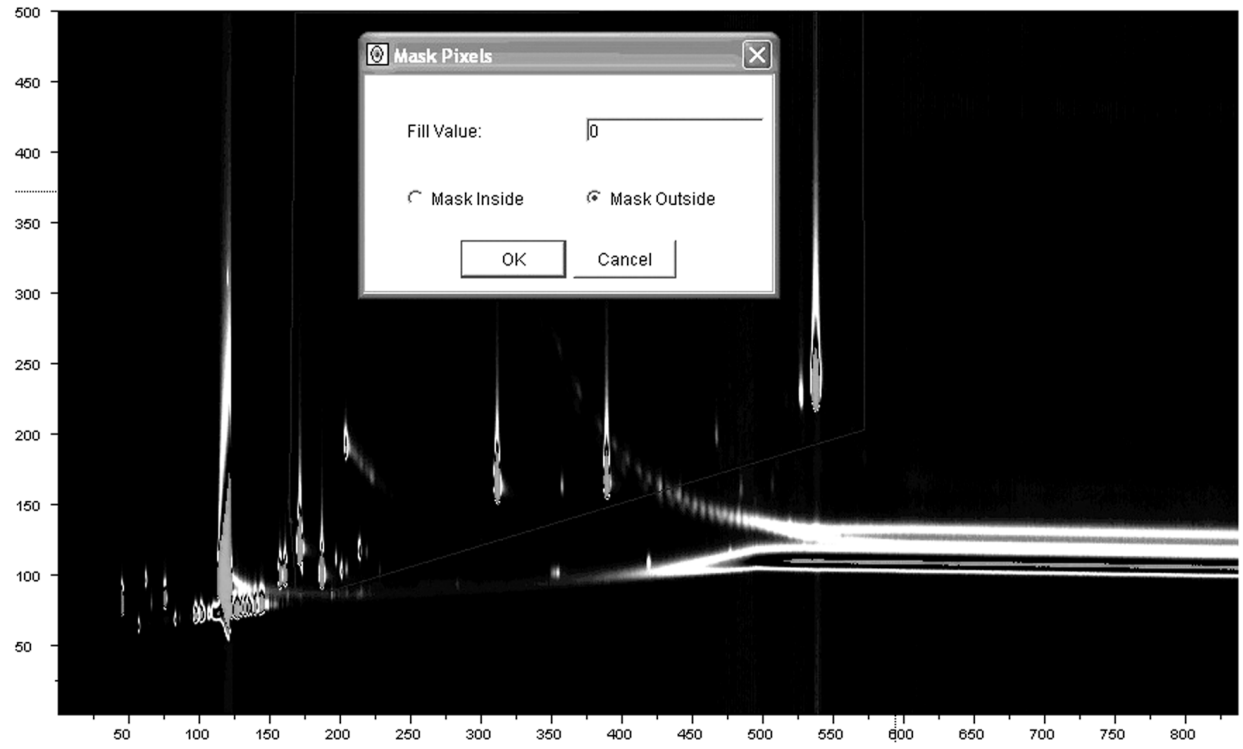

Figure 7. Masking signal/noise outside a polygon by GC image.

tionary phase, and column length on separation space and analyte elution order (19).

Figures 3A and 3B illustrate the effect of the primary column and temperature-programming rate on the GC×GC separations of alkanes and alkylbenzenes. For a given wax secondary column, the spacing between the alkanes band and alkylbenzenes band is approximately 0.5 s on the secondary dimension, as shown in Figure 3A using a primary column with a thick film of 1 µm and a relatively fast rate of 5°C/min. With a thin film of 0.25 µm in the primary column, a slow rate of 2°C/min, and a relatively high column flow rate of 1.2 mL/min (41 psig in Figure 3B vs. 18 psig in Figure 3A), the

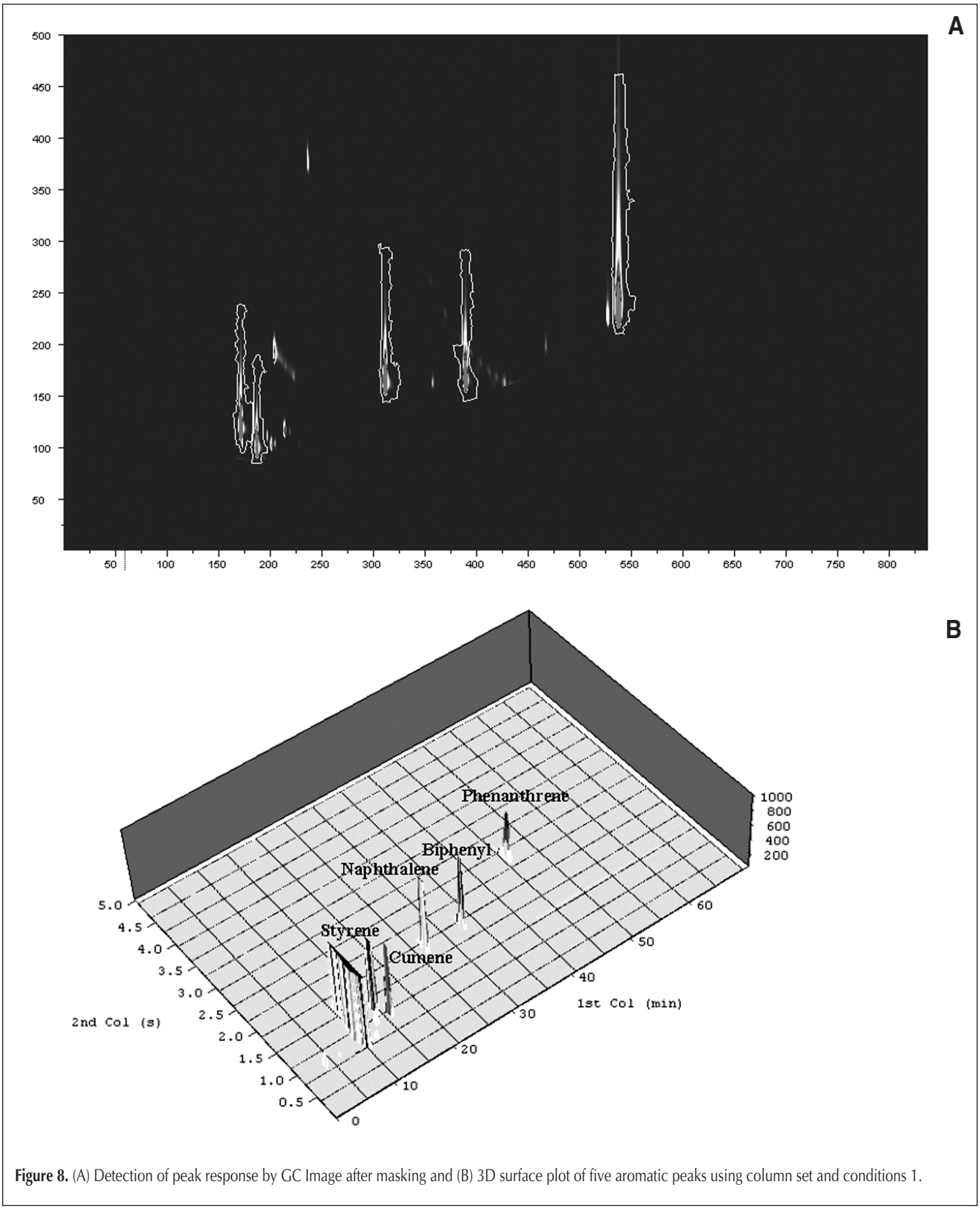

Figure 8. (A) Detection of peak response by GC Image after masking and (B) 3D surface plot of five aromatic peaks using column set and conditions 1.

spacing between the alkanes band and alkylbenzenes band on the second dimension is increased by approximately 3×, from 0.5 s to 1.5 s, except in the beginning of the chromatogram because of a higher initial oven temperature of 80°C. Because the solute elutes at a lower temperature on the secondary column using the column set and conditions 2, the polar solute capacity factor (k) in the polar wax stationary phase is increased.

As discussed previously, the GC×GC resolution for a given polar secondary column can be tuned to give different spacing on the secondary dimension. Figures 4 and 5 show contour plots of wash oils A and B using two different conditions. Much greater resolution was obtained using a thin film primary column and a slow temperature-programming rate, as shown in Figures 4B and 5B. However, for the group analysis of wash oils, the resolution provided by the conditions used to generate the chromatograms shown in Figures 4A and 5A is sufficient to quantitate the 1- and 2-ring aromatics content. Therefore, the lower resolution system of column set and conditions 1 was used, as shown in Figures 4A and 5A, to perform the quantitative analysis.

Integration of GC×GC peaks

The GC×GC data is displayed in a different way than one-dimensional GC. Generally, one displays three-dimensional GC×GC data in a contour plot. It is a challenge to integrate peak responses on a contour plot because GC×GC data are more complicated. So far, few papers have illustrated GC×GC quantitative analysis (12,20). Either a standard GC integration program or custom GC×GC program was used to integrate GC×GC peaks. Synovec et al. reported the determination of the concentrations of aromatic and naphthene compounds by multivariate quantitative analysis using trilinear partial least squares (21). For GC×GC analysis of a well-resolved simple mixture, one can use standard GC software (such as Agilent ChemStation) to integrate every modulated slice for each solute, then add all slices of each solute together to obtain total area for each solute, as shown in Figure 6A–E. Manual integration using Agilent ChemStation software was performed on every GC×GC modulated peak for five aromatic compounds: styrene, cumene, naphthalene, biphenyl, and phenanthrene. All five solutes were well separated, could be recognized visually on the GC×GC chromatogram, and were easily integrated by manual integration. Table I lists integration results.

In GC×GC chromatograms, the background noise includes all typical sources of noise (short-term, long-term, drift) seen in regular one-dimensional GC (22), plus modulated column bleed peaks. The modulated column bleed peaks can be a major source of background noise, particularly as the column temperature increases (shown in Figure 6E). The sharp peaks eluted just before the modulated phenanthrene peaks are typical column bleed peaks at high oven temperatures. Reichenbach et al. have discussed the background correction in GC×GC integration recently (23).

Integration results for the GC×GC analysis of a well-resolved simple mixture using the GC Image program to integrate peak responses were compared with results using a standard GC integration program to integrate peak areas. With the GC Image program, we performed the background correction with a default setting, then drew a polygon to circle all five solutes of interest. The GC Image allowed for masking all other signals outside the polygon to make the integration results simple (shown in Figure 7). This is somewhat like "Integration Off, On" in a regular integration program. Figure 8A is the resulting contour plot after masking. Finally, the responses of five solutes of interest in Figure 8B were integrated.

Table I lists integration results and normalized response percent using the GC Image and Agilent ChemStation. The normalized results were very close. For 4 of 5 solutes, the difference was less than 0.2%. For phenanthrene, a 1.6% difference has been determined. This discrepancy is likely caused by a high column bleed level at the high oven temperature and tailing peaks on the secondary dimension, as indicated in Figure 6E. Both of these have an impact on the accuracy of integration, but the difference is still relatively small.

Different units are used by GC Image and Agilent ChemStation, so absolute integration values vary. The ChemStation reports integration results with a unit of area pA × s, and the GC Image reports integration results with a unit of volume: pA × pixel (first dimension) × pixel (second dimension), or pA × time × time. The difference is equal to the sampling rate, which is 100× in this experiment in terms of response by GC Image/response by ChemStation, as shown in Table II.

For complicated GC×GC analyses with partially resolved peaks and trace signals, it is expected that GC×GC integration is more complicated.

Quantitation of aromatics content

Wash oils A and B were analyzed with column set and GC×GC conditions 1. Major components in wash oil B elute between n-C_{12} and n-C_{20}, and major components in wash oil A elute in the range of n-C_{12} to n-C_{16}. In general, we can group species into three bands: a nonpolar band, 1- and 2-ring aromatics bands, and a polyaromatic band (Figures 9 and 10). The contour plots in Figures 9 and 10 have been expanded to show more details in the area of interest. Note that Figures 9B and 10B show 3D surface plots in log 10 scale to display small and large peaks in the same plot.

Table II. Ratio of Response by GC Image/Response by ChemStation

Peak No.	Names	GC Image	ChemStation	Ratio
1	Styrene	216924.33	2168.96	100.0
2	Cumene	40646.76	405.96	100.1
3	Naphthalene	49920.66	498.90	100.1
4	Biphenyl	21729.08	216.81	100.2
5	Phenanthrene	29770.98	292.57	101.8
Total		358991.81	3583.19	100.2

The peak responses were integrated by the GC Image software, and relative amounts of aliphatics and 1- and 2-ring aromatics were estimated by response percent for each band. The results are listed in Table III. The relative standard deviations (n = 3) are 2.8% for aliphatics and 0.17% and 0.15% for aromatics. Wash oil A contains 10.4% aliphatics and 86.7% aromatics, wash oil B has a much higher concentration of 1- and 2-ring aromatics (99.1%), and saturated aliphatics are not detected.

Also, no evidence of high-level ppm of oxygenates can be observed in the polar region in the contour plots. This was

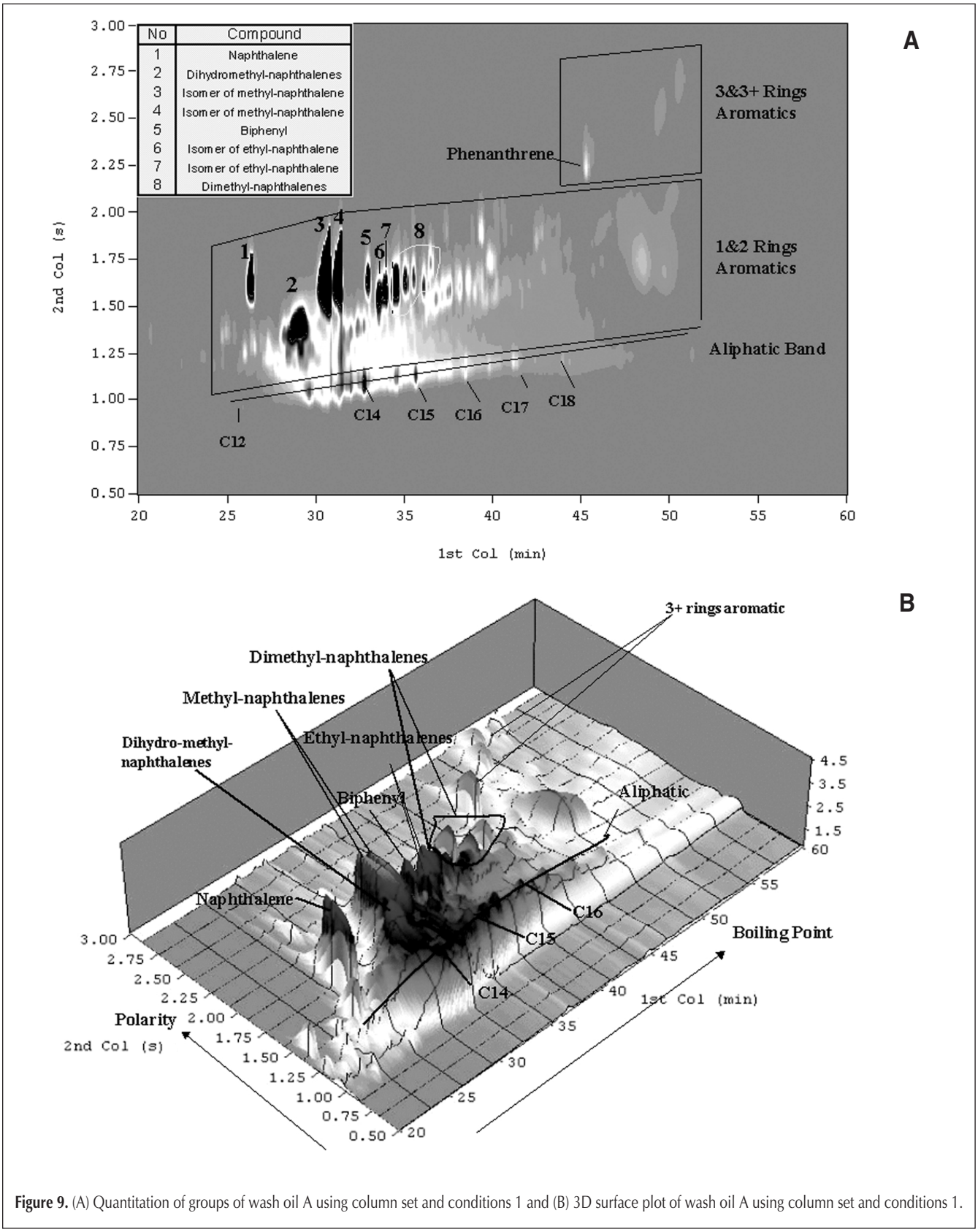

Figure 9. (A) Quantitation of groups of wash oil A using column set and conditions 1 and (B) 3D surface plot of wash oil A using column set and conditions 1.

confirmed using GC–AED to selectively detect oxygen-containing compounds at 171 nm. Representative GC–AED chromatograms are shown in Figures 11A and 11B. No detectable oxygenates (> 100 ppm) were found using the O-channel for both wash oils. Trace levels of sulfur-containing compounds were detected in Wash oil A, as indicated in the S-channel of Figure 11A.

These data show that wash oil B has a higher aromatics content and boiling point range than wash oil A, and could thus be an appropriate candidate to replace wash oil A.

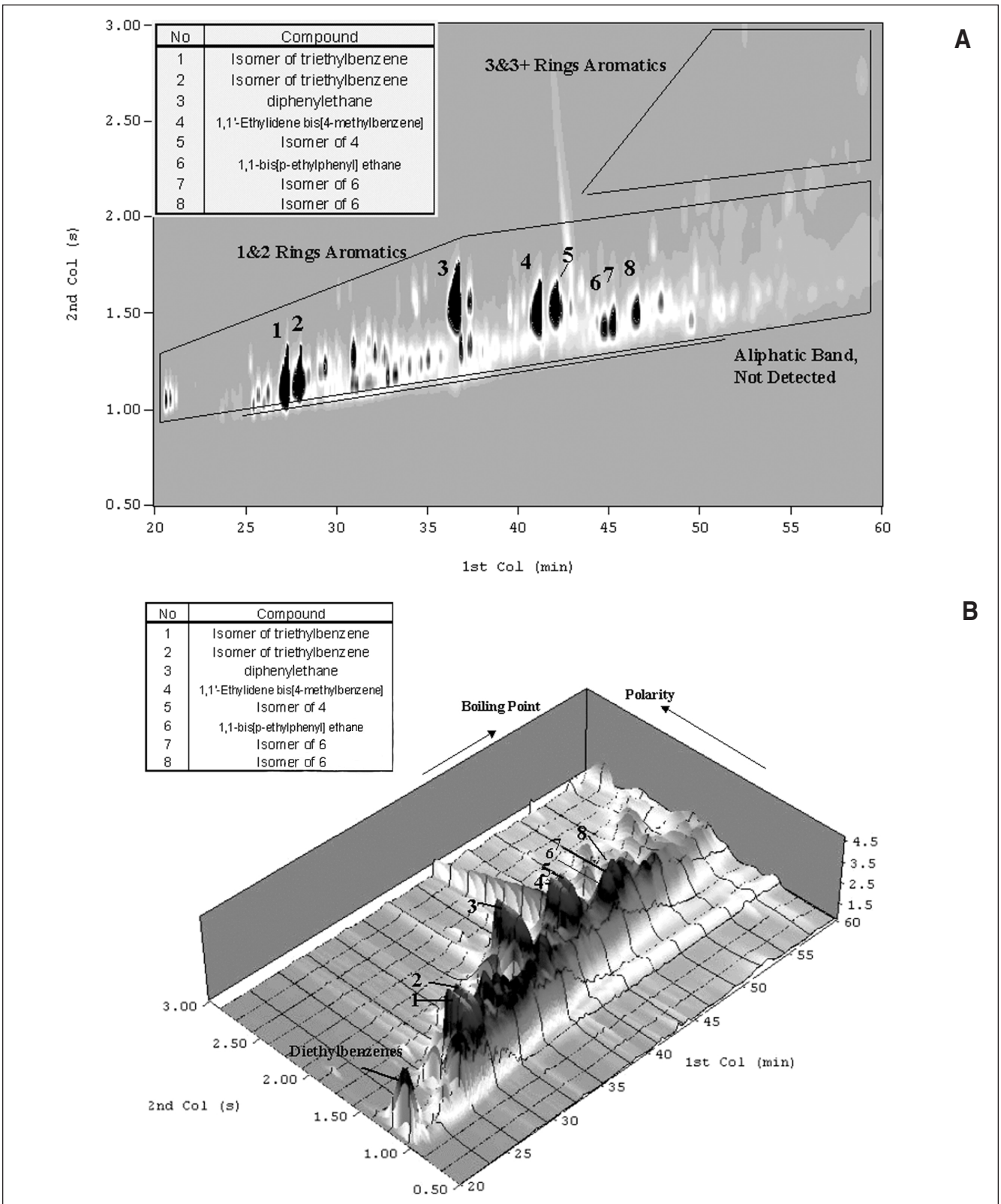

Figure 10. (A) Quantitation of groups of wash oil B using column set and conditions 1 and (B) 3D surface plot of wash oil B using column set and conditions 1.

Table III. Estimated Contents of Wash Oils A and B by Response Percent

	Wash oil A					Wash oil B				
	1	2	3	Average	%RSD*	1	2	3	Average	%RSD
Aliphatics%	10.5	10.0	10.6	10.4	2.8				ND†	
Aromatics%‡	86.8	86.7	86.5	86.7	0.17	99.0	99.3	99.2	99.1	0.15

* Relative standard deviation.
† Not Detected (< 0.0005%).
‡ 1- and 2-ring aromatics.

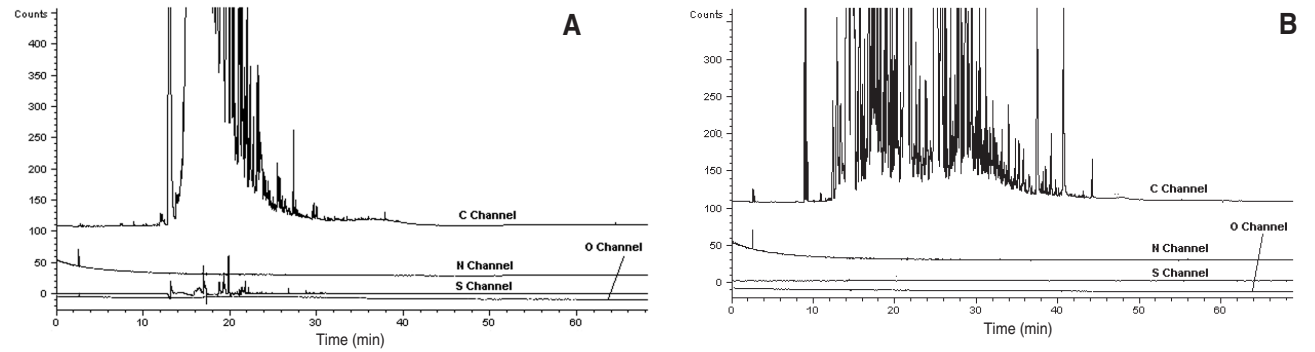

Figure 11. GC–AED chromatograms of wash oil A and (B) wash oil B.

Conclusion

A fast screening of wash oils without a need to identify individual peaks can be performed by GC×GC, which separates the samples into a nonpolar band, 1- and 2-ring aromatics band, and a polyaromatics band. The contents of aromatics and other bands can be estimated by peak response percent.

Tuning of a GC×GC system and integration of GC×GC peaks are keys to GC×GC quantitative analysis. Integration of peak response in GC×GC can be complex. For well separated GC×GC peaks, the conventional Agilent ChemStation GC software and the GC×GC software of GC Image give consistent integration results. For a given polar secondary column, the spacing of bands on the second dimension can be tuned in a broad region by changing capacity factors (*k*) of solutes on the secondary column. This can be accomplished by selecting a different film thickness for the primary column and a different temperature-programming rate.

Acknowledgments

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