Determination of aromatic hydrocarbons in gasolines by flow modulated comprehensive two-dimensional gas chromatography

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Abstract

Valve based/flow modulated comprehensive two-dimensional gas chromatography–flame ionization detection (GC × GC–FID) was used for quantification of C_6 through C_{12} aromatic hydrocarbons by carbon number in gasolines. A 0.53 mm i.d. non-polar first dimension column was coupled to a 0.53 mm i.d. polar second dimension column through a double loop eight port valve modulator. Depending on the sample type, normalized percent and internal standard (I.S.) quantification was performed. For normalized percent quantification, a one-point calibration performed with one aromatic compound per carbon number/class provided an average % accuracy of 2.1% and a short-term $n - 1$ relative standard deviation of 1.0%. For total aromatic compounds good agreement with the more complex conventional multidimensional GC technique was obtained. However, GC × GC has certain advantages over most other methods, mainly increased selectivity for total and carbon number aromatic content. The identification of the aromatic hydrocarbons was confirmed by GC × GC–MS.
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1. Introduction

The precise and accurate determination of aromatic hydrocarbons such as benzene as well as the level of total aromatic compounds in gasolines is important for control of refining processes and for government regulatory compliance. Comprehensive two-dimensional gas chromatography (GC × GC), where short time periods of effluent from a first dimension column are constantly transferred via a modulator to a second dimension column of different selectivity provides excellent separations of aromatic hydrocarbons (1–5). GC × GC has employed relatively advanced techniques, however, such as thermal modulation and state of the art instrumentation capable of fast acquisition rates of 100 Hz or greater. Thermal modulators are still undergoing refinements to increase their ruggedness and ease

of use. The relatively large amount of cyrogens such as carbon dioxide and liquid nitrogen required may limit, at least for the present, the applicability of thermally modulated GC × GC at certain industrial sites such as oil refinery laboratories. In addition, commercial quantitative software is at an early stage of development and acceptance for routine use. Seeley et al. have demonstrated, however, that GC × GC flow modulation can be performed by a valve [6], which is potentially a reliable approach without the need for cyrogens. Normalized percent quantitation of hydrocarbon mixtures by GC × GC-flame ionization detection (FID) has also been demonstrated with conventional software [1]. Presented below is the development and performance of a simple and rugged version of GC × GC for determining aromatic hydrocarbons in gasolines without interference from the many non-aromatic compounds present. This rugged approach has potential for implementation by production laboratories and for an improved methodology for regulatory use.

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2. Experimental

An Agilent Technologies 6890 gas chromatograph was configured as follows:

Injector: On-column. On-column injection was found to be five times more precise than split injection and to entail less maintenance and/or optimization.
Injector temperature program: 50 °C (0.1 min) 30 °C/min to 300 °C (until end of oven program).
Injection volume: 0.01 µl with an Agilent 7673C autosampler equipped with an SGE 0.5 microliter syringe and a nanoliter adapter.

Columns

First dimension: Agilent Technologies 60 m × 0.53 mm i.d., 5.0 µm film HP-1.
Carrier: Helium 2 ml/min for 110 min 99 ml/min to 60 ml/min until end of oven program.
Second dimension: Agilent Technologies 60 m × 0.53 mm i.d., 1.0 µm film DB-WAX.
Carrier: Helium at 50 ml/min.
Oven temperature program: 40 °C (0 min) 2 °C/min to 250 °C (15 min). Total run time = 120 min.

Detector

Flame ionization at 300 °C.
Hydrogen = 40 ml/min, air = 400 ml/min.
Data acquisition rate: 10 points/s (10 Hz).

Modulator description

A Valco DC8WT 1/16 in. (0.16 cm) eight-port valve (maximum temperature = 350 °C) was configured with two 5 ml gas loops as shown in Fig. 1A and B. Turning the valve on and off allowed effluent from the first dimension to alternately be collected in one of the two gas loops while the other loop was being swept into the second dimension. The valve was mounted in the standard valve oven of the gas chromatograph and pulsed on and off with a Valco AT45 air actuator controlled by a Valco digital valve interface and a Valco Digital Valve Sequence Programmer. A 1/8 in. (0.32 cm) gas lines with 50 p.s.i. (344.7 kPa) nitrogen were routed between the standard brass valve actuator on the GC oven and the AT45. The modulation interval was controlled by the sequence programmer, which was started and stopped by timed contact closures from the gas chromatograph. Columns were connected to the valve with Restek fused silica lined stainless steel tubing, Swagelok 1/16 in. (0.16 cm) unions and Supelco M2-A 1/16 in. (0.16 cm) graphite-vespel ferrules. The modulator was synchronized by adjusting the start signal (in this case to 0.55 min) until pentane, relatively unretained on Carbowax, eluted near the beginning of its respective second dimension interval. Since conventional one-dimensional chromatographic software was used for quantitation, this approach made processing simpler than shifting the relative position of the data after the acquisition. The modulation inter-

val of 1 min was confirmed by the elution of the compound, benzothiophene, the most retained aromatic compound in the boiling range under investigation. For simplicity of analysis, it was desirable to have this class of compound eluting at the end of a 1-min interval. Modulator discrimination was tested with an equal mass mixture of *n*-alkanes from C_5 through C_{12}. As expected with first dimension column flow, loop sizes and modulation interval used, no loss was found.
Valve temperature: 325 °C.
Data system
A Dell Omniplex 590 personal computer operating under Microsoft Windows 95 and Agilent Technologies A.04.02 ChemStation software was used for data acquisition, instrument control, and quantitation. Two-dimensional plots were obtained with Fortner Software Transform Version 3.4 after the signal files were exported in CSV file format by the ChemStation software.

2.1. Mass spectrometry

A Hewlett-Packard 5890 Series II gas chromatograph–5989A quadrupole mass spectrometer was equipped with a GC × GC system identical to that used for FID described above. An open-split interface [7] was used to couple the second dimension column to the MS and ensured that the elution order of the analytes was not affected by the mass spectrometer vacuum. Gas chromatographic conditions as described above.
MS parameters

Source temperature: 250 °C.
Analyzer temperature: 100 °C.
Ionization mode: positive ion, 70 eV electron impact.
Transfer line temperature: 260 °C.
Scan range: 40–185 u.
Scan rate: 4 spectra/s.

2.2. Calibration

Pure compounds were purchased from Aldrich (Milwaukee, WI, USA).
Calibration mixture: Table 1 describes the solution prepared for calibration.
This solution was used to generate a response factor for each carbon number. Indan was quantitated with the C_9-benzene (from 1,2,3-trimethylbenzene) response factor, C_{12}-napthhalenes were quantitated with C_{11}-naphthalene's response factor, and benzothiophenes were quantitated with naphthalene's response factor. Styrenes are often not at significant levels in gasolines (<0.01% m/m). They can be can be important components in steam cracked naphthas, however, and so styrene was included in the calibration mixture. Quantitation was by normalized percent for hydrocarbon streams with the response factor of the uncalibrated peaks or components set at 0.89. This value was de-
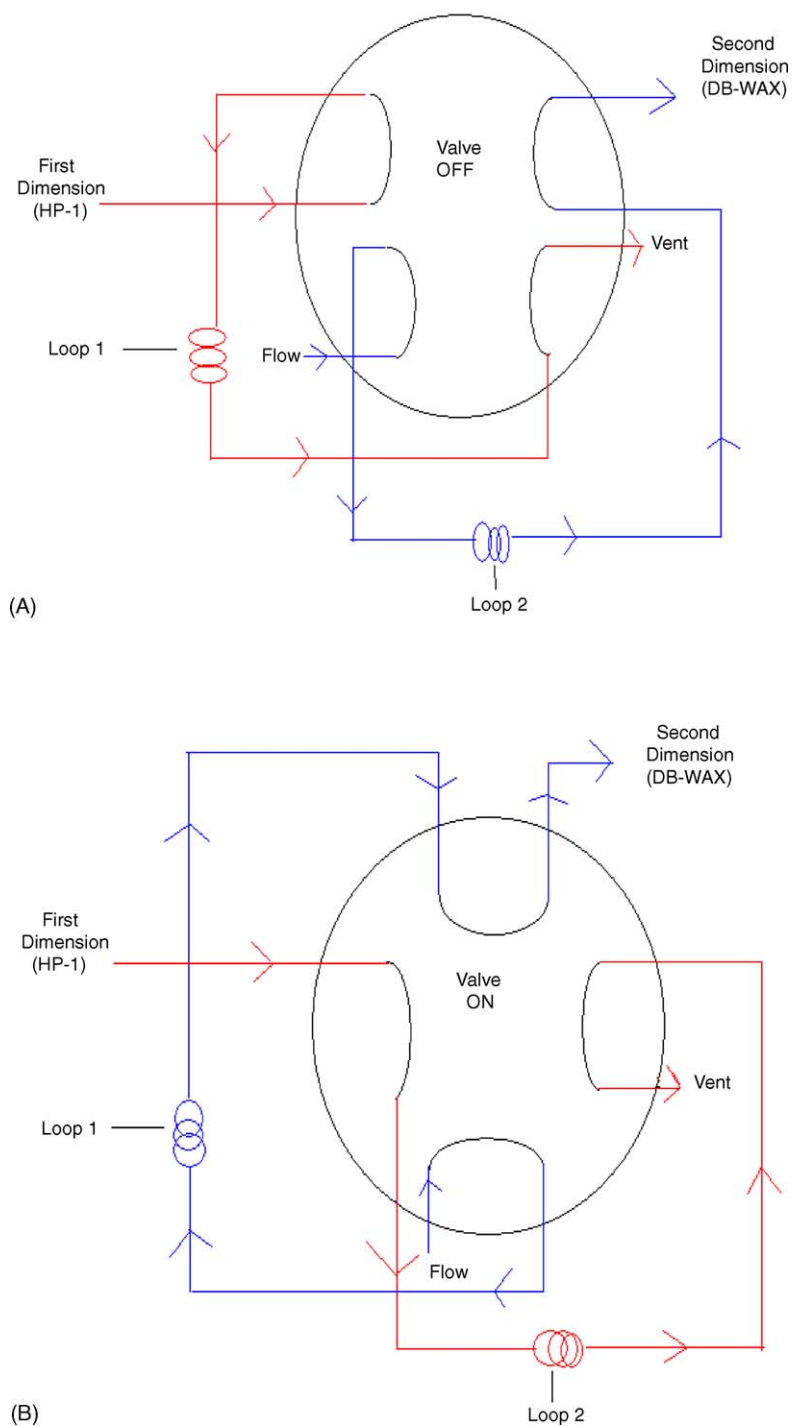
Fig. 1. (A) Flow modulation valve diagram showing valve in the off position. (B) Flow modulation valve diagram showing valve in the off position.

rived by adding aromatic compounds at known levels to a non-aromatic process stream called an alkylate (primarily isoalkenes) and varying the response factor for the highest accuracy.

Normalized percent quantitation was performed according to the following formula:

Mass % of aromatic component 'x'

$$= \left\{ \frac{A_x \mathrm{RF}_x}{[(\sum A_i \mathrm{RF}_i) + A_u 0.89]} \right\} \times 100$$

where A_x is the area of aromatic hydrocarbon of interest 'x'; RF_x the response factor of component 'x' = mass of 'x'/area

Table 1
Calibration mixture for normalized percent calibration

Compound	Mass ± 0.0001 g
Benzene	1.0
Toluene	10.0
Heptane	75.0
Ethylbenzene	5.0
Styrene	1.0
1,2,3-Trimethylbenzene	2.0
1,2,3,4-Tetramethylbenzene	2.0
Pentamethylbenzene	1.0
Hexamethylbenzene	1.0
Naphthalene	1.0
2-Methylnaphthalene	1.0

of 'x' for calibration mixture; A_i the areas of all aromatic hydrocarbons with a calibrated RF_i and A_u is the area of all uncalibrated no-aromatic hydrocarbons.

Hexamethylbenzene was used as an internal standard for fuels containing oxygenated blending components, such as ethanol. For the internal standard quantification, response factors for the calibrated aromatic hydrocarbons was obtained relative to the internal standard to obtain a total aromatic and aromatic carbon number distribution.

2.3. Sample preparation

For normalized percent quantitation: an autosampler vial was filled with neat sample and capped.
For internal standard quantitation: 2.0 g of sample were weighed into a screw cap vial to the nearest 0.0001 g. 0.20 g of internal standard, hexamethylbenzene, were weighed to the nearest 0.0001 g into the same vial. The solution was then placed into an autosampler vial and capped.

3. Results and discussion

Two widely used approaches are employed by the petroleum industry to produce selectivity for the relatively large numbers of aromatic hydrocarbons compounds present in gasolines. One of these approaches is multidimensional gas chromatography, such as ASTM D5580 [8] and the PIONA analyzer [9], and the other is gas chromatography coupled with either mass spectrometry or Fourier transform infrared spectroscopy [10,11]. Both approaches have been found to have limitations. ASTM D5580 is limited by interferences from C_{12+} alkanes and naphthenes [12] and the PIONA analyzer does not resolve accurately either C_{9+} aromatic compounds by carbon number or diaromatics. The GC–MS and GC–FT-IR approaches use the response factor of one compound for many of the C_{10+} aromatic compounds because calibration standards for the large number of isomers present are not commercially available for calibration of the two instruments. The latter techniques generate different and less accurate results than FID-based methods where the responses by carbon number have been found to be more uniform.
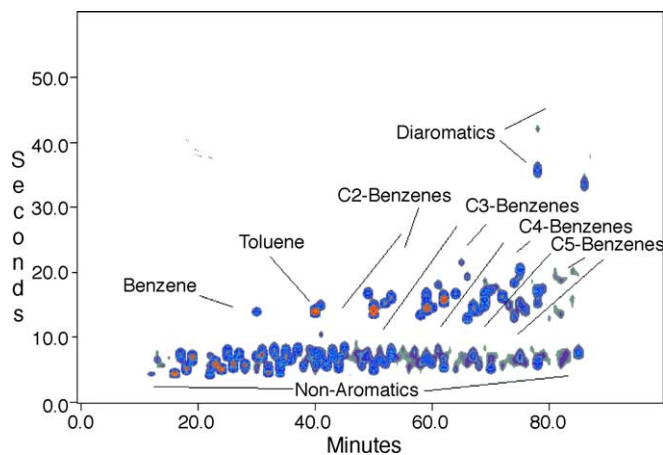

Fig. 2. Two-dimensional plot of GC × GC separation of gasoline. *x*-Axis: non-polar first dimension; *y*-axis: polar second dimension.

Fig. 2 shows the GC × GC separation of a gasoline on the system described above. Adequate resolution was obtained even though the 0.53 mm i.d. columns and the modulation conditions used were much different than those reported previously [1–6]. Note that all of the aromatic compounds were resolved by carbon number from the potentially co-eluting non-aromatic compounds and that the diaromatic compounds were also separated. Fig. 3 shows the detailed one-dimensional modulated chromatogram. Quantitative analyses was based on the areas of the peaks in the modulated one-dimensional data which was basically a series of 1 min second dimension separations beginning on the minute. Note that in each 1 min period, the non-aromatic compounds eluted first followed by the alkylbenzenes and then the diaromatic compounds. The software provided by the Agilent ChemStation was used for quantification. Group identifications, part of the standard software, were used to sum the aromatic compounds by carbon number into a final report. The retention time of the compound, *o*-xylene, was used to mark the end of the elution of C_8-benzenes. Indan was used to mark the end of the C_9-benzenes; 1,2,3,4-tetramethylbenzene was used to mark the end of the C_{10}-benzenes; pentamethylbenzene was used for the C_{11}-benzenes, and hexamethylbenzene was used for the end of the C_{12}-benzenes. These carbon number break points were confirmed by GC × GC–MS. Table 2 shows normalized percent precision and accuracy for a test

Table 2
Precision and accuracy data for normalized percent quantification

Compound/class	R.S.D. ($n-1$) (%)	Mean	Actual	% Accuracy
Benzene	1.2	1.19	1.22	2.5
Toluene	0.7	5.96	6.08	2.0
C_8-benzenes	0.2	2.36	2.46	4.1
C_9-benzenes	0.8	1.19	1.23	3.5
C_{10}-benzenes	1.4	1.25	1.26	0.8
Naphthalene	1.4	0.79	0.79	0.0

Results are in mass% (m/m), $n = 10$ over 2 days. Percentage accuracy = absolute value(mean − actual)/actual × 100. Average relative standard deviation = 1.0%. Average % accuracy = 2.1%.
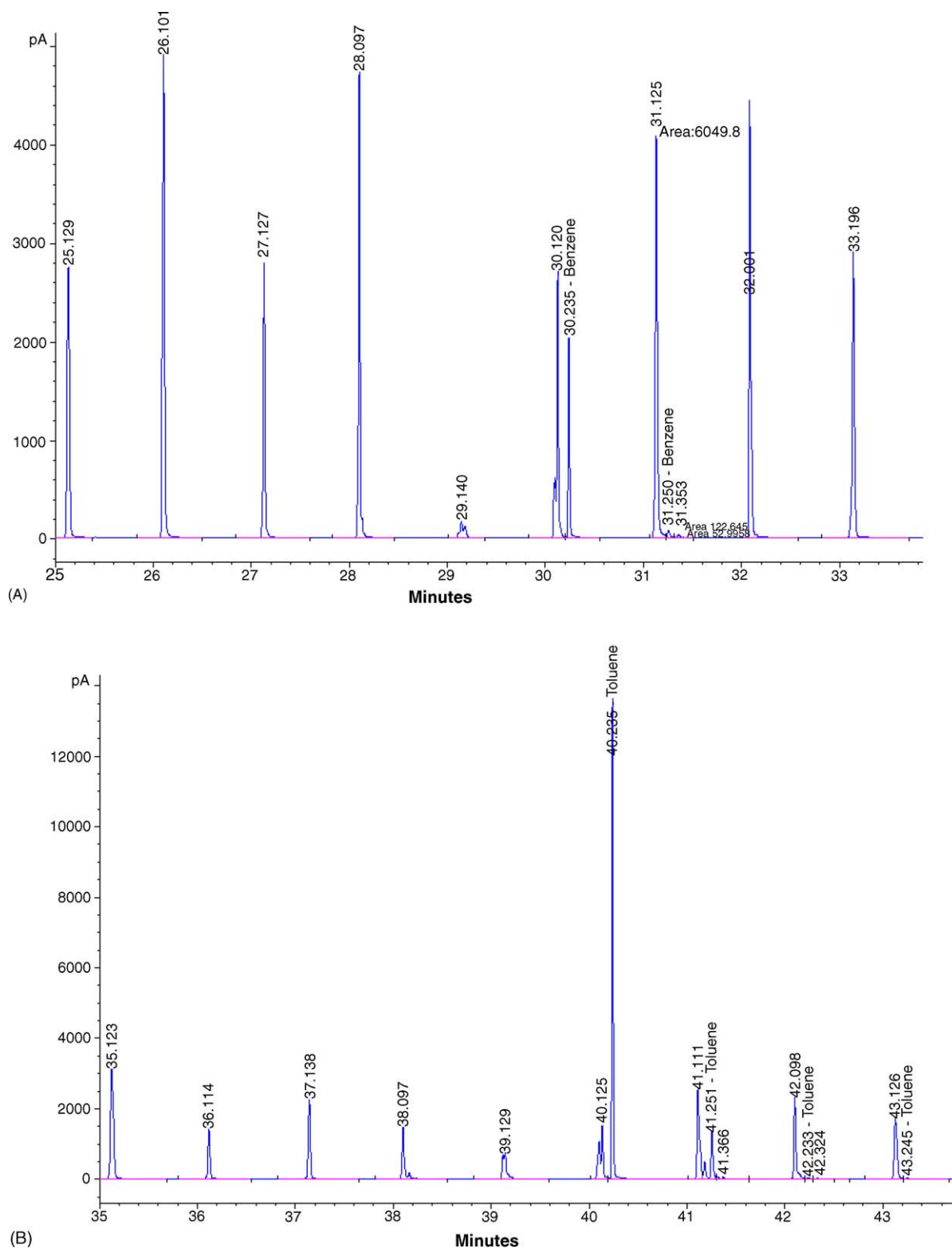
Fig. 3. One-dimensional plot of separation used for data analysis.

mixture of aromatics. The average % accuracy was 2.1%, and the average $n - 1$ relative standard deviation ($n = 10$ over 2 days) was 2.1%. Percentage accuracy was defined as: [(actual value − determined value)/(actual value)] × 100.

Table 3 shows the analyses of a fluidized catalytic cracking (FCC) gasoline by PIONA and by the GC × GC. Overall, the total aromatic compounds agreement was good. Note that there were differences in the C_9 and higher aromatic
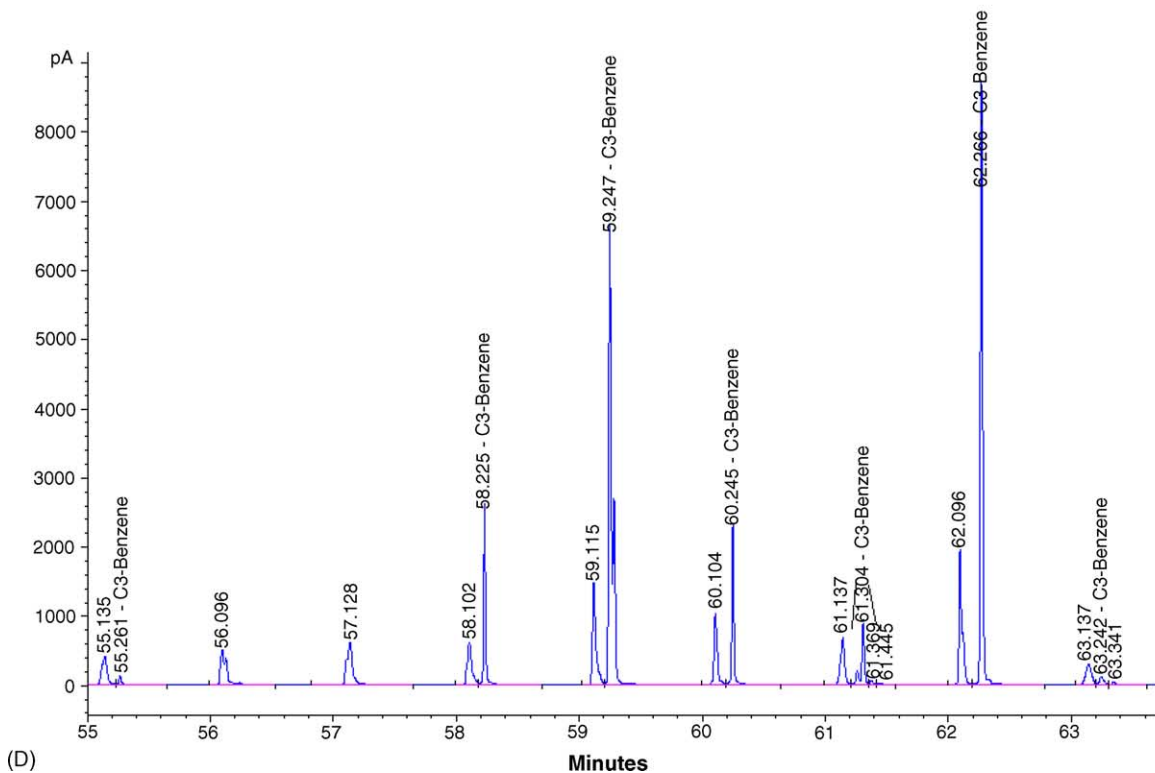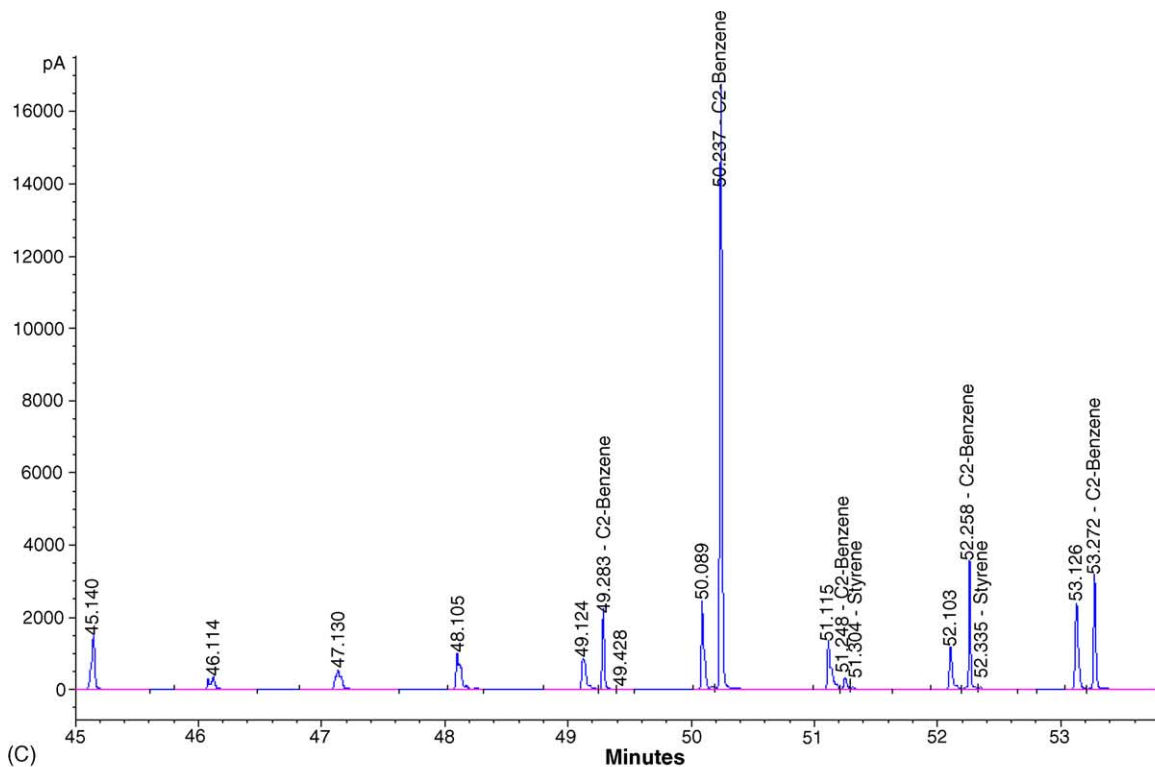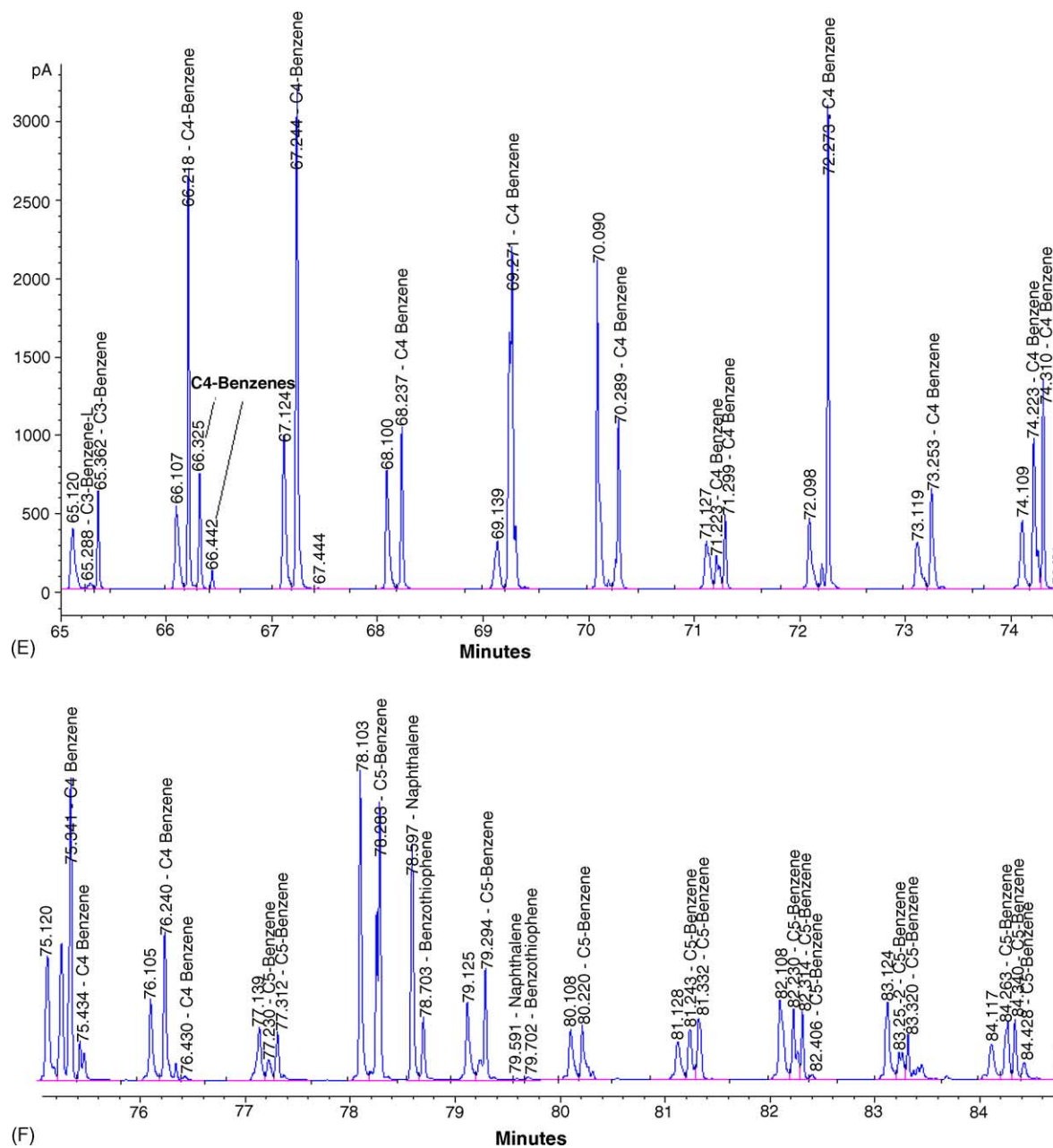
Fig. 3. (*Continued*)

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compounds. As mentioned above, the PIONA analyzer does not accurately report the distribution of the higher carbon number aromatic hydrocarbons and the data are often presented as total C_{9+} aromatic compounds.

To determine the precision of measuring total aromatics in a fuel, the FCC gasoline above was analyzed ten times over a 2-week period. This data is summarized in Table 4. The relative standard deviation of the total was 1.1%. Table 5 shows the analysis of an alkene-free naphtha compared with analysis by PIONA. Again, there was good agreement for total aromatic compounds.

Normalized percent quantitation was not a viable approach for gasolines, which contained oxygenated compounds such

Table 3
Analyses of an FCC naphtha

Compound/class	GC × GC	PIONA
Benzene	0.84	0.85
Toluene	4.42	4.40
C_8-benzenes	8.41	8.40
C_9-benzenes	9.39	7.60
C_{10}-benzenes	8.78	7.00
C_{11}-benzenes	2.60	Not reported
Diaromatic compounds	0.75	Not reported
C_{11+}-aromatic compounds	3.35	7.10
Total aromatic compounds	35.2	35.4

Results are in mass% (m/m).
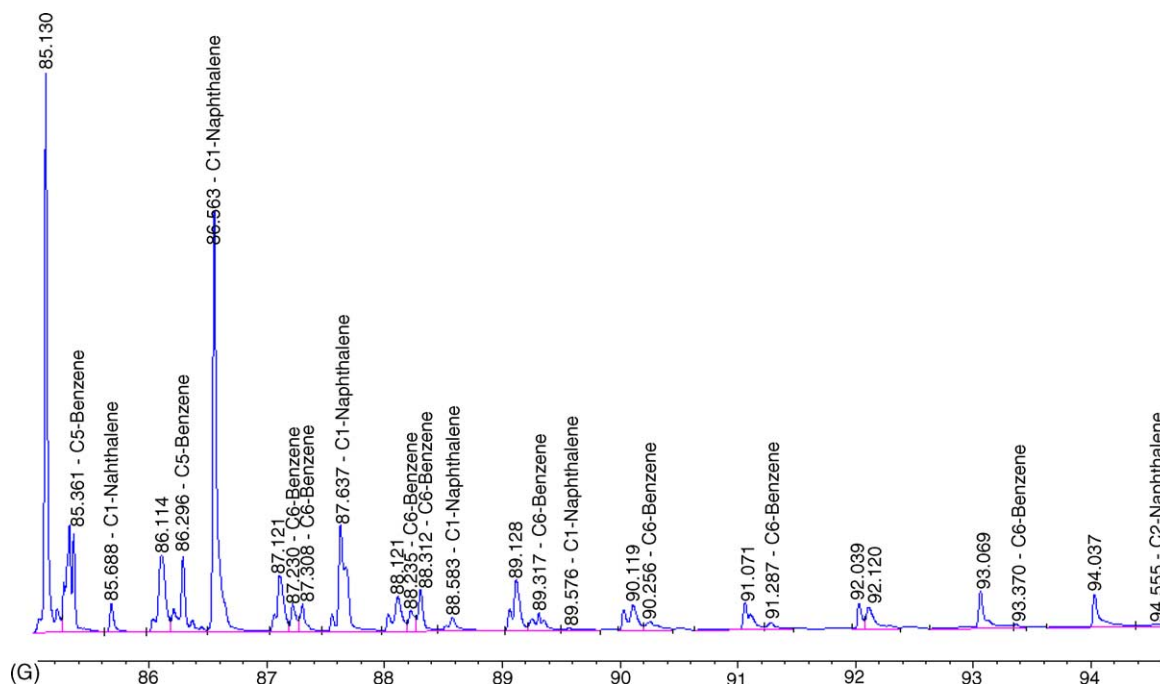
Fig. 3. (*Continued*).

Table 4
Total aromatics precision data

Compound/class	Mean	R.S.D. ($n-1$) (%)
Benzene	0.83	2.6
Toluene	4.40	0.5
C_8-benzenes	8.37	1.0
C_9-benzenes	9.38	1.4
C_{10}-benzenes	8.74	1.9
C_{11}-benzenes	2.61	1.8
Diaromatic compounds	0.72	3.0
Total aromatic compounds	35.1	1.1

Results are in mass% (m/m), $n = 10$ over 2 weeks. Average R.S.D. = 1.7%.

Table 6
Accuracy test using the internal standard approach for quantification

Compound/class	Determined	Actual	% Accuracy
Benzene	1.22	1.22	0.0
Toluene	6.10	6.08	0.3
C_8-benzenes	2.40	2.46	2.4
C_9-benzenes	1.28	1.23	4.1
C_{10}-benzenes	1.27	1.26	0.8
Naphthalene	0.76	0.79	3.8

Results are in mass% (m/m). % Accuracy = absolute value (determined − actual)/actual × 100. Average % accuracy = 1.9%.

as methyl-*tert*-butyl ether and ethanol. Ethers co-eluted with other non-aromatic compounds on the GC × GC system discussed here. Additionally, the response factors for oxygenates were much different than those of hydrocarbons. Applying the uncalibrated response factor of 0.89 to this class of compounds did not produce accurate results. As a result, hexam-

ethylbenzene was used an internal standard for oxygenated fuels. This compound eluted at two retention times or two modulation cycles, and the peaks were summed together with the manual integrator of the standard software for processing. Table 6 shows the analysis of an internal standard accuracy test mixture. The average % accuracy was 1.9%. Table 7

Table 5
Analyses of an allene free naphtha

Compound/class	GC × GC	PIONA
Benzene	1.00	1.00
Toluene	2.65	2.68
C_8-benzenes	4.67	4.79
C_9-benzenes	4.89	5.17
C_{10}-benzenes	2.01	1.23
C_{11}-benzenes	<0.01	<0.01
Diaromatic compounds	<0.01	Not reported
C_{11+}-aromatic compounds	<0.01	<0.01
Total aromatic compounds	15.2	14.9

Results are in mass% (m/m).

Table 7
Analyses of an oxygenated fuel

Compound/class	GC × GC	PIONA	GC–FT-IR
MTBE	Not reported	Not reported	15.11
Benzene	1.47	1.50	1.43
Toluene	5.37	5.40	5.51
C_8-benzenes	7.29	7.60	7.15
C_9-benzenes	6.12	5.80	Not reported
C_{10}-benzenes	2.93	2.60	Not reported
C_{11}-benzenes	0.53	Not reported	Not reported
Diaromatic compounds	0.28	Not reported	Not reported
C_{11+}-aromatic compounds	0.83	1.70	Not reported
Total aromatic compounds	24.0	24.7	Not reported

Results are in mass% (m/m).

shows the analysis of an oxygenated (methyl-*tert*-butyl ether, MTBE) fuel compared to PIONA and GC–FT-IR [11] results. GC–FT-IR was calibrated only for C_6 through C_8 aromatic compounds in addition to oxygenates. Fuels containing other oxygenates such as ethanol, which eluted well before benzene on the first dimension column and which did not interfere with the overall analysis of the aromatic hydrocarbons, could readily be analyzed by this approach.

4. Conclusion

Aromatic hydrocarbons in gasolines were precisely and accurately determined by carbon number with a rugged and simplified flow modulated two-dimensional gas chromatography system. This GC × GC approach has a number of advantages: (1) complete resolution, in a single analysis, over a wide carbon number of the aromatic hydrocarbons from non-aromatic components; (2) more accurate aromatic hydrocarbon carbon number distribution and a more accurate quantification for total aromatic compounds for a wider boiling point range over existing methods currently in use in the petroleum industry. The methodology can be implemented with existing instrumentation at a relatively low cost and without the need for software changes. Further enhancements to the methodology include shortening of the analysis time. Preliminary results indicate that the latter may be achieved by modifying the temperatures and flow operation of the two columns and using a shorter modulation period of 0.5 min. Results from the latter will be presented in the future.

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