Programmed Automation of Modulator Cold Jet Flow for Comprehensive Two-Dimensional Gas Chromatographic Analysis of Vacuum Gas Oils

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Abstract

A method is described for automating the regulation of cold jet flow of a comprehensive two-dimensional gas chromatograph (GC×GC) configured with flame ionization detection. This new capability enables the routine automated separation, identification, and quantitation of hydrocarbon types in petroleum fractions extending into the vacuum gas oil (VGO) range (IBP–540°C). Chromatographic data acquisition software is programmed to precisely change the rate of flow from the cold jet of a nitrogen cooled loop modulator of a GC×GC instrument during sample analysis. This provides for the proper modulation of sample compounds across a wider boiling range. The boiling point distribution of the GC×GC separation is shown to be consistent with high temperature simulated distillation results indicating recovery of higher boiling semi-volatile VGO sample components. GC×GC configured with time-of-flight mass spectrometry is used to determine the molecular identity of individual sample components and boundaries of different molecular types.

Introduction

The worldwide economic trend of limited supply and increased demand for crude oil has created need and incentive for the petroleum industry to process heavier feeds (measured as lower API Gravity) in order to obtain more value out of limited resources. Yield and quality of petroleum products from a refining process can be variable depending on feed and processing conditions. Measurement of the compositional changes from feed to product is essential in determining the effectiveness and optimization of a refining process. Improved characterization techniques can potentially lead the way to improvements in catalyst development and process design. Detailed compositional analysis can be used to design ways to eliminate catalyst fouling, improve understanding of catalytic reaction chemistry, and set improved specifications for quality products that better fit customer requirements (1).

The application of most analytical techniques for petroleum samples is usually limited to a specific limited boiling point range. For example, gas chromatographic detailed hydrocarbon analysis methods such as ASTM D 6729, D 6730, and D 6733 are very effective for separating and identifying the hundreds of individual components in spark ignition fuels (gasoline). Conventional vacuum gas oils (VGO) of nominal boiling range of 345 to 540°C (650–1000°F) are generally too complex to analyze by conventional gas chromatography and have been typically characterized by hydrocarbon group-type mass spectrometry techniques such as ASTM Test Methods D 2786 and D 3239.

Comprehensive two-dimensional gas chromatography (GC×GC) is an emerging technique well suited to complex samples, which can significantly expand the peak capacity, resolution, and sensitivity of a gas chromatographic analysis. With GC×GC the entire composition of a sample is subjected to two independent GC separations in a single analysis. A GC×GC instrument contains a coupled-column system with a modulator interfacing device to repetitively accumulate, focus, and re-inject sequential "heart-cut" fractions eluting from the initial GC column onto the coupled column. A GC×GC analysis is capable of separating a petroleum fraction into thousands of different components. The resulting separation can yield a great deal of information on molecular composition and hydrocarbon types present in a sample. If proper orthogonal chromatographic conditions are applied to many petroleum fractions, related sample components are arranged in a structured pattern, which enables group-type analysis and provisional classification of unknowns. There are a number of review articles on GC×GC (2–5) and publications on its application to petroleum fractions (6–9), and just recently it has been shown by adjusting the trapping temperature of the GC×GC modulator during sample analysis, one can extend the application of GC×GC into the vacuum gas oil boiling point range (10). This previous study defined temperature requirements for effective modulation of C_4 to C_{40} *n*-paraffins by cryogenic loop-type modulators to extend GC×GC analysis into the high C40 VGO range. In this work, we report the details of programming and automating the cold jet flow in a cryogenic loop modulator to enable the automatic routine unattended analysis of complex samples, such as VGO, with a very wide boiling point range.

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Experimental

Comprehensive GC×GC

GC×GC analyses were carried out using an Agilent 6890 gas chromatograph outfitted with an Agilent 6890 series automatic liquid injector, an auxiliary electronic pneumatic controller (Aux EPC), and flame ionization detector (FID) (Agilent Technologies, Wilmington, DE). The GC was also equipped with a CIS 4 Programmed Temperature Vaporizer (PTV) inlet (Gerstel, Mulheim an der Rühr, Germany) and a cryogenic loop modulator

assembly (Zoex KT2003; Zoex Corp., Houston, TX). A 230 L tank (Chart Cryogenic Systems, Cleveland, OH) was used to supply liquid nitrogen to both the cryo loop modulator and the PTV inlet. A Restek Rtx-1, 10.0-m length, 0.10-mm i.d., 0.40-µm film of 100% polydimethylpolysiloxane (Restek, Bellefonte, PA) was used for the primary GC separation. A SGE BPX-50, 1.0-m length, 0.10-mm i.d., 0.1-µm film of polysilphenylenesiloxane (SGE Analytical Science, Austin, TX) was used for the secondary coupled GC separation. The two columns were placed in the same temperature programmed oven. A 1.40-m length, 0.10-mm i.d., 0.1-µm thick deactivated silica transfer column (Restek) was used in the modulator to interface the primary column to the secondary column. All column-to-column connections were made with Agilent Ultimate Unions. Agilent ChemStation software was used for instrument control and acquisition of the raw chromatographic data from the flame ionization detector. Transformation, integration, and visualization of the GC×GC data were performed using Zoex GC-Image software. The specific gas chromatographic instrument conditions for GC×GC with FID detection are shown in Table I.

A separate GC×GC instrument configured with a LECO Pegasus 4D time-of-flight mass spectrometer (TOFMS) (LECO Corp., St. Joseph, MI) and CIS 4 Programmed Temperature Vaporizer (PTV) inlet (Gerstel) was used for peak identification. The GC×GC conditions (listed in Table II) were modified due to the differences in the modulator of the LECO instrument. The major differences in chromatographic conditions pertain to the modulator parameters and the addition of a secondary oven and temperature profile used for the secondary GC column. LECO Chroma-TOF software provided instrument control, data acquisition and transformation, integration, peak visualization, and display of the mass spectral data. Identifications were made by careful analysis of the mass spectral data and comparing them to a NIST library database. The software has a Peak Find algorithm to detect coeluting peaks in the total ion current chromatogram. A Mass Spectral Deconvolution algorithm provides accurate full range mass spectra free of coeluting analytes.

Cold jet nitrogen gas flow programming

The cold jet nitrogen gas flow rate of the Zoex cryo loop modulator was controlled with a gas mass flow controller (Model MC-20SLPM-D, Alicat Scientific, Tucson, AZ) which was spliced into the cold jet nitrogen gas supply line (see Figure 1). This was accomplished by making a cut in the hose that

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Table I. Gas Chromatographic Conditions for GC×GC–FID

GC×GC	Agilent 6890
PTV Temperature program	40°C initial, ramp 360°C/min to 340°C and hold
Split ratio	100:1
Injection volume for sample	0.10 µL
Primary GC Column	10.0-m length, 0.10-mm i.d, 0.40-µm film of polydimethylsiloxane (Rtx-1)
Secondary GC Column	1.0-m length, 0.10-mm i.d., 0.1-µm thick polysilphenylenesiloxane (BPX-50)
Modulator transfer column	1.40-m length 0.10-mm i.d., 0.1-µm thick deactivated silica column
Carrier gas	hydrogen
Column flow rate	0.4 mL/min, constant flow mode (22.43 psi @35°C)
Modulator hot jet temp	115°C initial, ramp 2.5°C /min to 340°C and hold
Modulator settings	300 ms hot jet duty cycle, 18 s period
FID temperatures	340°C
FID H2 flow	40 mL/min
FID air flow	550 mL/min
FID make up (nitrogen)	25 mL/min
GC oven programs	35°C initial, ramp 2.5°C /min to 340°C and hold
Data acquisition rate	100 Hz

Table II. Gas Chromatographic Conditions for GC×GC–TOFMS

GC×GC	Agilent 6890
PTV Temperature program	40°C initial, ramp 360°C/min to 340°C and hold
Split ratio	100:1
Injection volume for sample	0.5 µL
Primary GC Column	10.0-m length, 0.10-mm i.d., 0.40-µm film of polydimethylsiloxane (Rtx-1)
Secondary GC Column	1.8-m length, 0.10-mm i.d., 0.1-µm thick polysilphenylenesiloxane (BPX-50)
Carrier gas	hydrogen
Column flow rate	0.4 mL/min, constant flow mode
Modulator hot jet temp	80°C initial, ramp 1.2°C /min to 340°C and hold
Modulator cold jet temp	6 lpm
Modulator settings	2.60 s hot jet duty cycle, 24 s period
GC primary oven program	35°C initial hold 0.2 min., ramp 1.2°C /min to 340°C and hold 18 min.
GC secondary oven program	50°C initial, ramp 1.2°C /min to 340°C and hold
MS	Pegasus 4D TOFMS
Detector transfer line temp	340°C
Ionization	EI at 70 eV
Mass Range	50 to 680 u
Acquisition Rate	100 spectra/s
Source Temperature	225°C

Figure 1. Automated modulator cold jet flow rate control.

directly attached to and supplied the nitrogen gas cooled by the liquid nitrogen Dewar. The nitrogen supply end of the cut hose was attached to the inlet of the gas mass flow controller while the other cut hose end was attached to the outlet of the gas mass flow controller. The gas mass flow controller was set specifically for nitrogen gas and the flow rate setting was input and regulated electronically from a separate pressure gauge (Model P-30PSIG-D, Alicat). An RS-232 cable was used to supply signal of the pressure gauge to the gas mass flow controller. The inlet of the pressure gauge was attached to a nitrogen gas line connected to an Aux EPC of the GC instrument. The outlet of the pressure gauge was attached to a 2-m length, .010-inch i.d., stainless-steel tubing bleed line. The pressure gauge monitored back pressure from the Aux EPC which was controlled remotely via Agilent ChemStation software. A 5% solution of ASTM Test Method D 2887 calibration mix (AccuStandard, New Haven, CT) in carbon disulfide was used to tune and program the GC×GC–FID instrument modulator cold jet flow rate.

GC high-temperature simulated distillation

High-temperature simulated distillation analyses were carried out according to ASTM Test Method D7213 using an Agilent 6890N chromatograph configured with a flame ionization detector (Analytical Controls, now PAC, Houston, TX) and equipped with an AC Temperature Programmable Inlet (PTV). A capillary column (SGE BPX1-SIMD, 6 m × 530 µm i.d. × 2.65 µm film of 100% dimethylpolysiloxane) was used for the GC separation. An extended D2887 simulated distillation standard (containing a mixture of n-paraffins, C_5–C_{60} dissolved in carbon disulfide) was used to determine the boiling point versus retention time relationship over the boiling point range required by the method. Agilent ChemStation software was used for instrument control and acquisition of the raw chromatographic data from the FID. The simulated distillation method calculations were performed using an AC SIMDIS software package. The specific GC instrument conditions for high-temperature simulated distillation are shown in Table III.

Sample preparation

Vacuum gas oil samples were prepared by first heating them to approximately 80°C for 5 min. An aliquot of the sample was then diluted by weight at a ratio of up to 4:1 carbon disulfide–sample. The diluted samples were shaken by vortex mixer to facilitate dissolution.

Results and Discussion

The goal of this study was to extend the routine unattended operation of GC×GC analysis of petroleum fractions into the vacuum gas boiling range. Table IV lists the various parameters considered in developing and optimizing the GC×GC method. A hindrance in the application of GC×GC for the analysis of higher boiling petroleum fractions has been the

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Table III. Gas Chromatographic Conditions for High Temperature

Simulated Distillation

Instrument	Agilent 6890N (configured by AC)
PTV Temperature program	40°C to 350°C at 15°C/min
Injection volume	1 µL
GC Column	6 m × 0.53 mm × 2.65 µm, BPX1-SIMD (SGE)
Carrier gas	hydrogen
Column flow rate	28 mL/min, constant flow mode
FID temperatures	390°C
FID H2 flow	35 mL/min
Air flow	350 mL/min
GC oven program	–10°C to 375°C at 15°C/min, hold 7 min
Data acquisition rate	50 Hz
Sample dilution	2 wt % in carbon disulfide
Calibration dilution	1 wt % in carbon disulfide

Table IV. GC×GC Method Parameter Considerations for Extending Into VGO Boiling Point Range

GC×GC Method Parameter	Considerations
Instrument selection	Readily adaptable to cold jet flow programming
Column selection	One boiling point column, one polarity column; both thermally stable to 340°C
Column dimensions (length, i.d., and film thickness)	Optimized for sample recovery with sufficient resolution and sample capacity
Column fittings	Applicable to column dimensions, rugged, reliable and easy to install
Carrier gas	Optimum efficiency with minimal analysis time
Sample solubility	Soluble at ambient temperature and concentration suitable for detection of trace components
Sample size (injection size and inlet split flow)	Detect trace components and resolve analytes of interest
GC Inlet	Avoid cracking of heavier compounds and sample component discrimination
GC Oven temperature profile	Separate and recover wide sample boiling range (i.e., 36 to 565°C)
Programmed control of modulator cold jet temperature	unattended operation

thermal limit of the polar polywax column, which is typically used in the analysis of naphtha and diesel range samples. For this study, a secondary column with a 0.1-µm thick-bonded phase of polysilphenylenesiloxane was selected as they are commercially available with programmable stability up to 340°C. This was deemed practical because greater than 345°C some petroleum components can begin to decompose as the energy needed to evaporate the high-molecular weight molecules exceeds the energy required to break carbon–sulfur, carbon–nitrogen, or carbon–carbon bonds. Cracking or coking of sample components may result particularly with prolonged heating, leading to erroneous analytical results. The next obstacle was to determine the appropriate column dimensions on a boiling point column and a carrier gas linear flow velocity that could elute the upper boiling range of the vacuum gas oil at or before a final temperature of 340°C. It was found that a 10.0-m length, 0.10-mm i.d. column with 0.40-µm film of polydimethylsiloxane [operated in a constant flow mode of 0.4 mL/min (hydrogen carrier gas)] could effectively elute n-alkanes up to C_{44} before reaching the final temperature of 340°C. Holding at that temperature for an additional 20 min, the elution of n-alkanes up to C_{48} was observed. The short column length and thin film thickness enable the elution of higher molecular weight compounds at a boiling point several hundred degrees below their atmospheric equivalent boiling point. This is consistent with what others have found for high-temperature simulated distillation analysis and
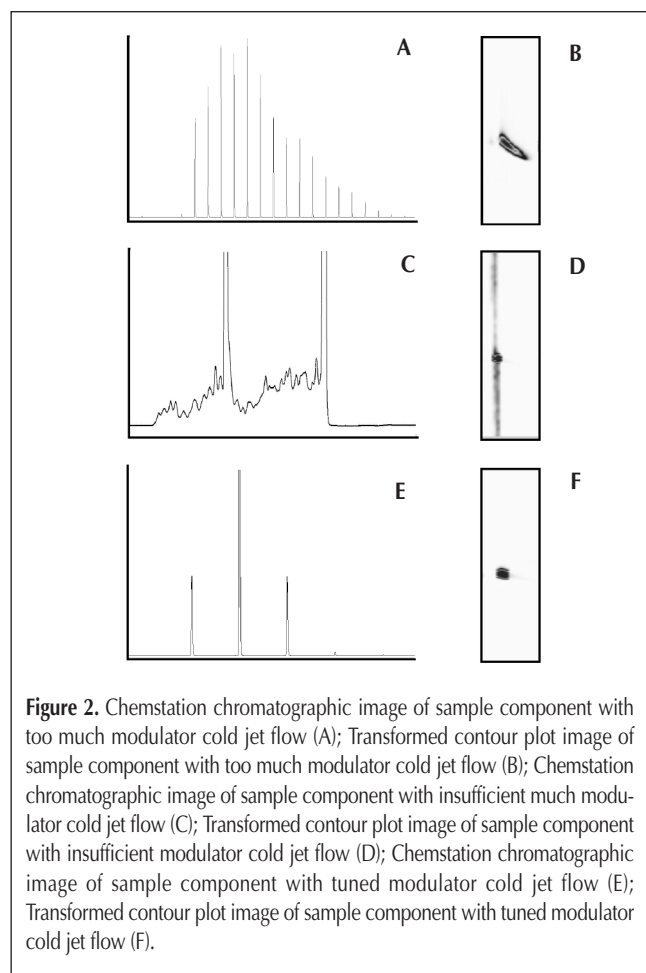
for analysis of materials beyond the distillate range (10). The potential disadvantages of the column geometry are lower 1st dimension resolution and lower sample capacity, requiring samples to be of wider boiling point range distribution or else significantly diluted. A final inlet back-pressure of 47.8 psig was typically observed with the combination of columns selected and listed in Table I. Higher flow velocities would result in higher inlet back-pressures and a chromatographic system more prone to leaking.

It has been reported previously that the typical cold jet flow rate used for modulating naphtha or distillate boiling range materials is excessive for semi-volatile compounds that boil above n-C26 (10). Excessive modulator cold jet flow rates causes either irreversible trapping or delayed releasing of sample material. There is a failure to launch of the cryo-focused material from the modulator. On a transformed contour plot image, it is typically observed as peak-tailing, particularly along the x-axis (Figure 2B). The symptom can be subtle and often observed only at higher concentrations in peaks that are sufficiently resolved from other sample components. In a non-transformed chromatogram, it is observed as extra modulated peaks eluting beyond the typical elution boiling point of the compound (Figure 2A). Coincidentally, this is also the same symptom of column overloading, which is associated with the shorter capacity secondary columns typically used for GC×GC. Alternatively, insufficient modulator cold jet flow rates can result in both fronting and tailing of peaks (see Figure 2C). This is observed on a transformed contour plot image as peak tailing along the y-axis (Figure 2D). In this case, the modulator temperature was insufficient for capturing or focusing the entire volatile compound. One can demonstrate a range of conditions when the cold flow is not enough and the effects observed vary dependent upon concentration of the analyte. For a highly volatile compound with no cold flow you will observe no modulation. The peak will elute as that normally observed on a conventional GC analysis. As one increases cold flow, a fraction of the analyte will start to modulate, resulting in fronting and tailing between the modulated peaks. The fronting and tailing is a result of the lack of tempera-
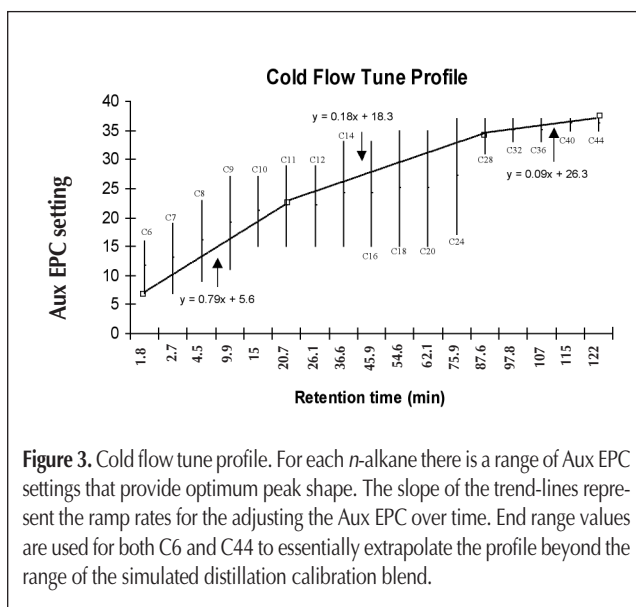

Figure 2. Chemstation chromatographic image of sample component with too much modulator cold jet flow (A); Transformed contour plot image of sample component with too much modulator cold jet flow (B); Chemstation chromatographic image of sample component with insufficient much modulator cold jet flow (C); Transformed contour plot image of sample component with insufficient modulator cold jet flow (D); Chemstation chromatographic image of sample component with tuned modulator cold jet flow (E); Transformed contour plot image of sample component with tuned modulator cold jet flow (F).

Figure 3. Cold flow tune profile. For each n-alkane there is a range of Aux EPC settings that provide optimum peak shape. The slope of the trend-lines represent the ramp rates for the adjusting the Aux EPC over time. End range values are used for both C6 and C44 to essentially extrapolate the profile beyond the range of the simulated distillation calibration blend.

ture needed to capture and refocus the entire analyte. One eventually reaches a temperature and concentration of the analyte in which the tailing ends and is captured, focused, and launched appropriately. These are common symptoms observed when analyzing samples that contain components that vaporize below the boiling point range or scope of a GC×GC method. A proper modulator cold jet flow rate will elute peaks in a Gaussian shape pattern (Figure 2E), which will appear as a focused peak, with minimal peak tailing, on a transformed contour plot image (Figure 2F).

In a typical GC×GC instrument, the modulator cold jet flow rate is controlled by a flow restrictor (regulator on gas cylinder) following the nitrogen gas supply which is set to a single specified pressure setting to provide the same cold jet flow rate through out the entire chromatographic analysis. The extension of the scope of GC×GC into a higher boiling range (i.e., beyond C_{26}) requires the capability to adjust the flow rate of the cold jet during the run. A GC×GC instrument with a cryo-loop modulator assembly (Zoex Corporation) was selected as it could be easily reconfigured for cold jet flow rate programming. The precise control and monitoring of the cold jet flow was accomplished by adding a gas mass flow controller in line after the regulated nitrogen gas source and prior to the liquid nitrogen Dewar used to cool the nitrogen gas (see Figure 1). The gas mass flow controller can be controlled remotely via a pressure gauge attached to an auxiliary electronic pneumatic controller (Aux EPC) of the GC. In this configuration, a higher pressure setting entered for the Aux EPC results in higher pressure monitored by the pressure gauge, which communicates with the gas mass flow controller to reduce the flow rate for nitrogen gas to the cold jet of the modulator. By slowly increasing the pressure of the Aux EPC during the course of an analysis, one can effectively modulate higher boiling semi-volatile compounds that require slower modulator cold jet flow rates. For automated analysis, a means was necessary to reduce the higher pressure exerted from the auxiliary EPC at the end of an analysis. This was accomplished by

attaching a restrictive bleed line to the pressure gauge. The length and diameter of the bleed line was selected such that it would maintain much of the accumulated pressure during the course of a sample analysis and yet bleed off the excess pressure within the time (several minutes) it takes for the GC oven to cool to the specified temperature for the subsequent sample analysis. The back-pressure measured by the pressure gauge was within 14 psig of the pressure entered by the Aux EPC at the highest EPC setting. At the highest programmed EPC setting (i.e., 37), a flow rate of approximately 21 mL/min was measured from the bleed line of the pressure gauge.

The precise control and programming of the gas mass flow controller is affected by adjusting the pressure setting on the Aux EPC during the course of an analysis. Agilent ChemStation software allows for the programming of up to four Aux EPC settings and three different ramp rates in a single data acquisition method. This was found to be sufficient to provide the appropriate cold jet flow rate profiles. The goal, ultimately, is to precisely control the temperature at the thermal focal points of the modulator by varying cold jet flow. Because the focusing of the cold flow in any individual cryo loop modulator is not precisely specified, there is potential for variation and, therefore, each cold jet flow rate profile must be specifically programmed and tuned to each individual instrument set-up. This was accomplished by first recording the nitrogen gas flow rate readings from the gas mass flow controller over a range of Aux EPC settings from 1 to 41. Then a 5 vol-% solution of a simulated distillation standard (containing *n*-alkanes from C_6 to C_{44}) in carbon disulfide was analyzed multiple times using odd number Aux EPC settings from 1 to 41, and the other chromatographic conditions listed in

Table V. Tuning of Cold Flow Programming

Carbon #	Ideal Aux EPC (psig)	Ideal flow (SLPM)
nC6	7–16	25.0–19.0
nC7	7–19	25.0–17.0
nC8	9–23	23.7–14.3
nC9	11–27	22.4–11.5
nC10	15–27	19.8–11.5
nC11	15–29	19.8–10.2
nC12	15–29	19.8–10.2
nC14	15–33	19.8–7.4
nC16	15–33	19.8–7.4
nC18	15–35	19.8–6.0
nC20	15–35	19.8–6.0
nC24	17–37	18.4–4.6
nC28	31–37	8.8–4.6
nC32	33–37	7.4–4.6
nC36	33–37	7.4–4.6
nC40	35–37	6.0–4.6
nC44	35–37	6.0–4.6

Table VI. Aux EPC Cold Jet Flow Program

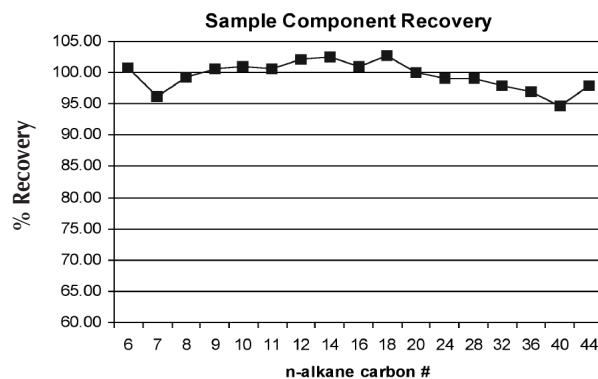| Time	Aux EPC (psig)	Ramp (psig/min)
Initial	7	0.79
20.7	22	0.18
87.6	34	0.09
121.8	37	hold

Figure 4. Sample component recovery of an ASTM Test Method D 2887 calibration mixture.

Table I. Table V shows the Aux EPC settings and associated nitrogen gas mass flows measured, respectively, that provided optimal peak shape (i.e., best symmetry with minimal tailing) for each n-alkane. The retention times (boiling point axis) for the individual n-alkanes of the simulated distillation standard were recorded, and an Aux EPC pressure profile was determined that would provide the optimum gas flow rates over the course of the chromatographic separation. The data was plotted as shown in Figure 3. A modulator cold jet flow profile was constructed by using the lower range of nC_6, the middle range of both nC_{11} and nC_{28}, and the upper range of nC_{44}. The slopes between the four individual Aux EPC settings were then calculated, which represent the ramp rates between the Aux EPC settings. The four individual Aux EPC settings and three ramp rates (see Table VI) define the modulator cold jet flow profile which were entered into the ChemStation chromatographic acquisition data method.

A programmable thermal vaporizer (PTV) inlet operated in split mode was used to provide optimal transfer and injection of
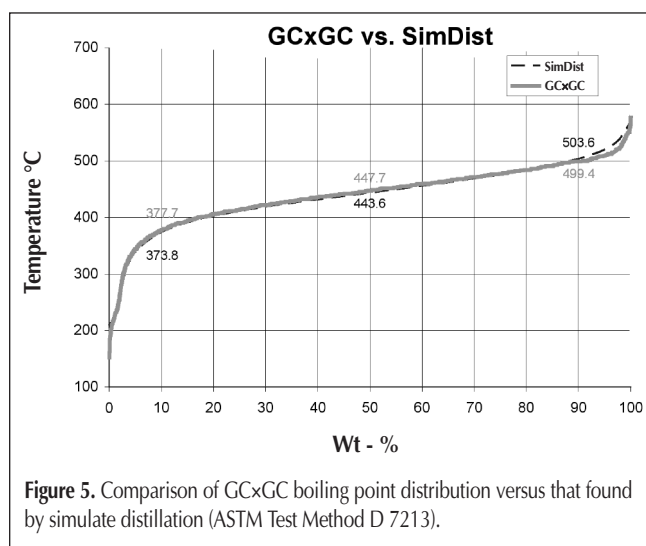
the VGO samples and minimize sample component discrimination. The PTV inlet enables one to avoid potential cracking of sample components by not introducing them at a high initial temperature and is often recommended in high temperature simulated distillation methods such as ASTM D6352, D7169, and D7213. Experimentation with simulated distillation standards indicated that the best recovery of n-alkanes was accomplished by injecting the sample at 40°C (slightly above the primary GC oven temperature) and ramping rapidly (360°C/min) up to the final oven temperature of 340°C. Figure 4 shows the % recovery of the different n-alkane compounds found in a simulated distillation calibration blend, analyzed according to the chromatographic conditions listed in Table I.

Sample recovery

In order to evaluate total sample recovery of the GC×GC method, beyond just n-alkanes, a comparison was made of the boiling point distribution found from a typical VGO separation from that reported from the simulated distillation analysis of the same material by ASTM Test Method D 7213. The chromatographic elution times of the separated components from the GC×GC analysis were indexed to the atmospheric equivalent boiling points of n-alkanes (C_9 to C_{48}) detected in the GC×GC analysis. This was done using Kovat's retention indices to reference each peak in the chromatogram in boiling point order. Figure 5 shows the comparison of the cumulative wt-% boiling point distribution obtained by both GC×GC and simulated distillation. Boiling point values determined at 10, 50, and 90 wt-% by GC×GC (displayed in Table VII) were found to be within the reproducibility of D 2887. A reproducibility statement for D 7213 was unavailable.

Figure 6 (See Page 5A) is a typical two-dimensional chromatogram contour plot image of a straight run VGO feed analyzed according to the chromatographic conditions listed in Table I. Retention time in the first dimension (boiling point separation) is shown on the x-axis; retention time in the second dimension (polarity separation) is shown on the y-axis. The two GC separation mechanisms create a structured chromatogram that enables the classification of the different sample compounds into molecular type chemical classes. The cold jet flow program provides for symmetrically focused peaks across the entire boiling range of the analyzed sample.

The identification of the peaks in any typical vacuum gas oil boiling range sample is a daunting task considering the enormous number of possible compounds that can be present, taking into account the various hydrocarbon types, heteroatomic species, and wide carbon number range. For example, it has been reported that the potential number of just paraffin isomers calculated at a carbon number of 45 equals 8.22×10^{15} (1). Another obstacle to the task is that the spectral database libraries are extremely limited within the VGO boiling range. One may however simplify the task by extrapolating the identified patterns of hydrocarbon types known in naphtha and middle distillate boiling range samples. For example, Figure 7 (See page 5A) is a contour plot total ion current image of the lower boiling range

Figure 5. Comparison of GC×GC boiling point distribution versus that found by simulate distillation (ASTM Test Method D 7213).

Table VII. Comparison of GC×GC and ASTM D7213 Boiling Point Values

Wt-%	Difference in values (°C) (GCxGC) vs. ASTM D7213	Repeatability of D7213 (D2887)	Reproducibility of D2887
10	3.9	2.58 (0.8)	7.9
50	4.1	3.36 (1.0)	4.3
90	4.2	2.76 (1.0)	4.3

Table VIII. Repeatability of the GC×GC Method

Hydrocarbon type	Mean	Standard Deviation
Paraffins, olefins, and naphthenes	44.2	0.26
1 ring aromatics	19.3	0.24
2 ring aromatics	15.5	0.34
3 ring aromatics	8.4	0.19
4+ ring aromatics	12.6	0.49

naphthalene region of a straight run VGO sample analyzed by TOFMS. In this region the pattern and identity of individual naphthalenes can readily be determined and that information translated to FID contour plot images. The spectral data obtained from TOFMS was also useful in aiding in the interpretation of molecular type boundaries on the chromatographic image even though often the searched compound was not in the spectral reference library. Some individual hydrocarbon types have been imaged with selective extracted ion traces. The LECO Chroma-TOF software used also has the capability of using Microsoft VBScripting language for even more selective data filtering based on abundance, rank, intensity, starting, and end of the presence of specified masses detected in the mass spectra. Complete identification of the molecular species present in any given VGO sample will continue to be a work in progress for some time to come. With these considerations, Figure 8 (See page 5A) is a contour plot image of the same straight run VGO feed sample in which a template has been applied to identify the boundaries of 1, 2, 3, and 4 plus ring aromatics present in the sample. With the applied template, the integrated volumes of the peaks found within specified boundaries were summed to indicate the mass-% of the hydrocarbon types present in the sample. The results were normalized to 100%, assuming complete recovery of the entire sample for detection by FID. Table VIII shows the repeatability of the methodology based on the analysis of one sample six times with the same operator.

One must use caution, however, in interpreting the GC×GC results, as they are susceptible to much interference from olefins, polynaphthenes, and heteroatomic species. The different hydrocarbon type boundaries converge and overlap at higher boiling points. All of the compound classes at least partially overlap in the VGO boiling range and accuracy of results will depend upon template selection. Results have been found to be consistent with HRMS measurements, but require correction depending upon what type of the interfering species are present.

Conclusions

The modulator cold jet flow programming scheme described in this paper has been successfully used to automate the analysis of samples with a boiling point range of C_5 (36°C) to C_{48} (565°C). This helps optimize separation and resolution of VGO sample components in both the first and second dimension that can elute across a wide boiling range. Comparisons made with simulated distillation analysis indicate satisfactory recovery of sample components with minimal discrimination. Identification of sample components in the analysis is aided by the use of TOFMS. More selective detector schemes or prior sample fractionation may be required to correct for interference from heteroatomic or other coeluting species. Whereas accuracy and bias of this

methodology has not been fully determined the technique has been found to be useful for monitoring changes in sample composition.

References

1. K.H. Altgelt and M.M. Bodusznski. *Composition and Analysis of Heavy Petroleum Fractions.* Marcel Dekker, Inc., New York, NY, 1994.
2. J. Dallüge, J. Beens, and U.A.Th. Brinkman. Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool. *J. Chromatogr. A* **1000:** 69–108 (2003).
3. J. Blomberg, P.J. Schoenmakers, and U.A.Th. Brinkman. Gas chromatographic methods for oil analysis. *J. Chromatogr. A* **972:** 137–173 (2002).
4. J.B. Phillips and J. Beens. Comprehensive two-dimensional gas chromatography: a hyphenated method with strong coupling between the two dimensions. *J. Chromatogr. A* **856:** 331–347 (1999).
5. T. Górecki, J. Harynuk, and O. Panic. The evolution of comprehensive two-dimensional gas chromatography (GC×GC). *J. Sep. Sci.* **27:** 359–379 (2004).
6. C.Vendeuvre, R. Ruiz-Guerrero, F. Bertoncini, L. Duval, D. Thiebaut, and M. Hennion. Characterisation of middle-distillates by comprehensive two-dimensional gas chromatography (GC×GC): A powerful alternative for performing various standard analysis of middle-distillates. *J. Chromatogr. A* **1086:** 21–28 (2005).
7. G.S. Frysinger, R.B. Gaines, and E.B. Ledford, Jr. Quantitative determination of BTEX and total aromatic compounds in gasoline by comprehensive two-dimensional gas chromatography (GC×GC). *J. High Resol. Chromatogr.* **22(4):** 195–200 (1999).
8. J. Beens and U.A.Th. Brinkman. The role of gas chromatography in compositional analyses in the petroleum industry. *Trends Anal. Chem.* **19(4):** 260–275 (2000).
9. V.G. van Mispelaar, A.K. Smilde, O.E. de Noord, J.Blomberg, and P.J. Schoenmakers. Classification of highly similar crude oils using data sets from comprehensive two-dimensional gas chromatography and multivariate techniques. *J. Chromatogr. A* **1096:** 156–164 (2005).
10. R.B. Gaines and G.S Frysinger. Temperature requirements for thermal modulation in comprehensive two-dimensional gas chromatography. *J. Sep. Sci.* **27:** 380–388 (2004).