



Short communication

Overcoming the high-temperature two-dimensional gas chromatography limits to elute heavy compounds

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ABSTRACT

Overcoming high-temperature (HT) two-dimensional gas chromatography (GC×GC) limits is critical for the analysis of heavy hydrocarbons, particularly those contained in heavy petroleum fractions. To reach this goal, HT-GC×GC analysis was adapted from HT-GC Simulated Distillation (HT-GC SimDist) operating conditions as this analysis embraces compounds whose boiling point ranges from 35 °C to 700 °C and from a previous study that enabled the elution of linear alkane nC_{60} and tetraaromatic compounds by HT-GC×GC. This paper shows that HT-GC×GC analysis using CO₂ cryogenic modulator and short wide bore columns with a thin film of stationary phase allows the elution of linear alkanes up to nC_{68} (641 °C) as well as of highly aromatic hydrocarbons like coronene. Furthermore, compared to previous studies, an on-column injector was used to reduce discrimination of high boiling point compounds.

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1. Introduction

HT-GC×GC refers to all analyses whose final oven temperature is higher than 340 °C [1]. This technique allows the elution of heavy compounds without pre-treatment (*i.e.* derivatization) by increasing the final oven temperature and by adapting chromatographic conditions. However, the main requirement is that both compounds and columns must be thermally stable at those temperatures.

Columns thermal stability is indeed a great issue in HT-GC×GC especially for polar stationary phases. The most thermally stable mid-polar column (BPX-50, 50% phenylpolysilphenylenesiloxane, SGE, Keynes, United Kingdom) allows oven temperatures as high as 370 °C while non-polar columns can reach temperatures as high as 400 °C. Recent advances in terms of stationary phases chemistry offer some exciting possibilities for the development of new HT-GC×GC methods. For instance, specific treatments of sol-gel phases [2] and GC stationary phases based on ionic liquids [3] have been recently introduced. They exhibit a better separation efficiency at high temperature than regular phases despite the fact that they are not stable above 300 °C yet and therefore not adapted to HT-GC×GC experiments. Consequently, improvement of polar phases is still required and expected.

The injection mode and the modulation device are also critical for the GC×GC analysis of heavy compounds. Firstly, cold on-column injection is usually chosen as it eliminates discriminations towards most non-volatile compounds [4]. Programmed-temperature vaporization injection (PTV) is also adapted to the analysis of many high boiling point compounds [5]. Secondly, adsorption of heavy compounds is likely to occur when excessively cold temperature are used for the modulation [6]. A CO₂ cryogenic modulator is usually recommended as it provides “warmer” cold jets (−30 °C to −60 °C) [7] than a N₂ cryogenic modulator (−180 °C) [8]. N₂ cryogenic modulator needs programmed cold jet flows in order to use colder jets for volatile compounds and slightly less cold ones for non-volatile compounds [6,9].

Operating conditions (columns dimension, temperature rate, gas flow rate and modulation period) are the most influencing parameters for GC×GC of heavy compounds [10]. Dutriez et al. [11] evidenced that column dimensions are the main parameter to optimize. The selection of a suited set of capillary columns is based on four factors: the nature of the stationary phase, the column diameter, the film thickness and the column length. These parameters can indeed be adapted so that compounds can elute sooner from the first column and reach the second column at a lower temperature [12]. Thanks to these observations, Dutriez et al. [11] succeeded in eluting hydrocarbons up to nC_{60} (615 °C) and tetraaromatic compounds in vacuum gas oils (VGO) samples. The authors used a non-polar first column (DB1-HT) to separate compounds according to their boiling point and a polar second column (BPX-50) to separate compounds by polarity. The phase ratio of the

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first column ($^1\beta=800$) enabled the elution of linear alkanes until nC_{60} . A lower phase ratio ($^2\beta=250$) was used for the second column and hydrocarbons containing up to four aromatic rings were eluted during one period of modulation. However, compounds containing more than four aromatic rings underwent wrap-around. Furthermore, major discriminations of heavy linear alkanes due to the use of a splitless injector were noticed and a discrimination factor was used to quantify hydrocarbons in VGO samples.

The aim of the study is to handle compounds having boiling point above 615 °C in HT-GC×GC and to elute highly aromatic compounds without any discrimination and wrap-around.

2. Experimental

2.1. Chemicals

A Fischer-Tropsch wax provided by IFP Énergies Nouvelles was spiked with linear alkane nC_{46} and used to evaluate the elution properties of the chromatographic system. Fischer Tropsch process converts coal, natural gas and low value refinery products into high value clean products. Linear alkanes are the main products of this process. Other products like branched alkanes, alcohols and olefins can also be formed. Before the analysis, the sample was diluted in CS_2 (approximately 100 ppm, w/w).

To evaluate the elution properties of the chromatographic system, a standard mixture was prepared using commercially available hydrocarbons which are representative of the compounds contained in VGO samples. These compounds were obtained from Sigma-Aldrich (Lyon, France) and are listed in Table 1. This test mixture was prepared in CS_2 with a concentration of 80 ppm (w/w) per compound.

Analysis gases, helium (99.999%), air and hydrogen (99.999%) were provided by Air Liquide (Pierre-Bénite, France).

2.2. HT-GC×GC-FID experiments

HT-GC×GC experiments were carried out using an HP 6890 GC (Agilent Technologies, Massy, France) hyphenated to a Flame Ionisation Detector (FID), equipped with a CO_2 dual jet modulator and an on-column injector. A constant flow rate

(3 mL/min) of helium, close to the optimum velocity of the first column, was used as the carrier gas. The 2D modulation period was set to 20 s. The on-column injector was set to 90 °C with a temperature program until 400 °C and a ramp of 100 °C/min. The oven was set to 90 °C with a temperature rate of 2 °C/min to 370 °C. The FID detector was set to 370 °C with a hydrogen flow of 35 mL/min, an air flow of 400 mL/min and a helium make up flow of 35 mL/min. The study was carried out by combining a non-polar first capillary column DB1-HT 10 m × 0.53 mm × 0.15 μ m (dimethylpolysiloxane, J&W, Folsom, Keynes, USA) and a mid-polar second capillary column BPX-50 0.5 m × 0.2 mm × 0.05 μ m (50% phenylpolysilphenylene-siloxane, SGE, Keynes, United Kingdom).

Raw data of FID detector signal were acquired using the HP Chemstation software (Agilent Technologies, Massy, France) and exported as a CSV-file for GC×GC data processing. GC×GC contour plotting, retention time measurement, blob fitting and peak integration were performed using 2D ChromTM (Thermo Scientific, Courtabœuf, France). Intensities are displayed via contrasting colors, ranging from pale blue to dark blue that represent respectively minor and major peaks.

3. Results and discussion

High temperature conditions are required in order to analyze high boiling point compounds by gas chromatography (GC or GC×GC). To succeed in this challenging technical procedure, all GC components, especially columns, must be adequately chosen. Various operating conditions must indeed be adapted to reach our goal while keeping in mind that maintaining an equilibrium between the loss of elution at high temperature and the desired high separation efficiency is critical [11].

3.1. Optimization of the operating conditions

HT-GC SimDist (ASTM D6352) is a high temperature technique that enables the elution of compounds in the order of their boiling point up to 700 °C (e.g. boiling point of linear alkane nC_{90}). A wide bore non-polar column (DB-HT SimDist, 0.53 mm) with a thin film of stationary phase (0.05–0.15 μ m), resulting in a high phase ratio (β), is required to elute high molecular weight compounds.

An increase of the phase ratio means that the retention factor of the compound decreases so a high phase ratio is needed to elute compounds at a lower temperature. In HT-GC SimDist, the phase ratio ranges between approximately 800 and 2600. Furthermore, column bleeding is reduced with thin films of stationary phase and short columns are recommended to elute low-volatile compounds. The corresponding operating conditions are detailed in Table 2.

Table 1
Composition of the test mixture.

Linear alkanes		Boiling point (°C)
1	nC_{26}	412
2	nC_{32}	466
3	nC_{38}	509
4	nC_{44}	545
5	nC_{50}	575
6	nC_{54}	592
7	nC_{60}	615
Monoaromatics		
8	C ₁₈ -benzene	408
9	C ₂₀ -benzene	429
10	C ₂₄ -benzene	502
Diaromatics		
11	C ₈ -biphenyl	382
12	C ₁₀ -biphenyl	410
Triaromatics		
13	Anthracene	340
14	2-tert-Butylanthracene	376
Tetraaromatics		
15	Pyrene	404
16	Benzanthracene	438
Pentaaromatics		
17	Perylene	468
18	Dibenzanthracene	518
Heptaaromatic		
19	Coronene	525

Table 2
Operating conditions obtained from the literature and optimized in this study.

	Operating conditions		
	HT-GC-SimDist	Dutriez et al. [11]	This work
First column	DB-HT SimDist	DB1-HT	DB1-HT
Length	10 m	10 m	10 m
Diameter	0.53 mm	0.32 mm	0.53 mm
Film thickness	0.05–0.15 μ m	0.1 μ m	0.15 μ m
Phase ratio	2650–883	800	883
Second column		BPX-50	BPX-50
Length		0.5 m	0.5 m
Diameter	–	0.1 mm	0.2 mm
Film thickness		0.1 μ m	0.05 μ m
Phase ratio		250	1000
Injector	On-column	Splitless	On-column
Modulator	–	Cryogenic CO_2	Cryogenic CO_2

The first step of our work was to choose the most appropriate column set to elute heavy compounds and the most thermally stable one in order to set the final oven temperature as high as possible. DB1-HT is a non-polar column used in HT-GC SimDist experiments that is thermally stable until 400 °C. Moreover, this column showed good performances in the analysis of heavy petroleum fractions like vacuum gas oils [11,13]. Thus, DB1-HT was selected as the first dimension column of our chromatographic system. The choice is much more complicated for the second dimension column as a polar column is needed. BPX-50 which is a mid-polar column was chosen as its final temperature of use is 370 °C. This column set allows us to raise the final oven temperature up to 370 °C.

In GC×GC analysis, the elution temperature of the compounds eluted from the first column is also the temperature of the second dimension separation. This separation is considered as isothermal during the modulation period since it lasts only a few seconds. The second step is therefore to adapt the geometry of the first column in order to elute compounds sooner from the first column so that they can reach the second column at a lower temperature. Compared to Dutriez et al. [11], a phase ratio higher than 800 was implemented in order to elute heavier compounds than nC_{60} . A short second column (0.5 m) and a long 2D modulation period (20 s) are needed as elution temperatures of the first column are reduced. A wide bore first column (0.53 mm) is therefore required to fulfill the Murphy bidimensional criterion of 3 or 4 modulations per peak [14]. However, these capillary columns are extremely complicated to produce and the thinnest film of stationary phase commercially available for an internal diameter of 0.53 mm is 0.15 μm . This gives a maximum phase ratio of 883. This column was therefore chosen as our first dimension column. To go further, wide bore capillary columns (0.53 mm) with a stationary phase thinner than 0.15 μm could be used to increase the phase ratio and elute even higher boiling point compounds. Consequently, improvement of stationary phases geometry is still required and expected.

In a similar way, the next step was to use a high phase ratio for the second column so that hydrocarbons with more than four rings could be eluted during a single modulation period. This is also required because due to the reduction of the elution temperature in the first dimension systematic wrap-around occurs in the second dimension. Thus, a high phase ratio ($^2\beta = 1000$) was chosen for the second column owing to the increased retention in the second dimension.

According to literature, an on-column injector and a CO₂ cryogenic modulation were used in order to avoid both discrimination and adsorption of high boiling point compounds. All the operating conditions are listed in Table 2.

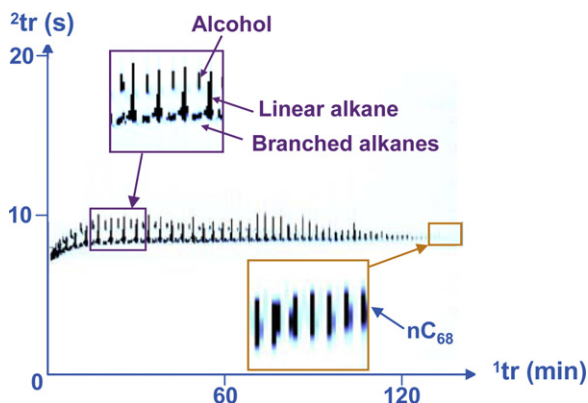


Fig. 1. 2D contour plot of the Fischer Tropsch wax (see experimental conditions in Section 2.2).

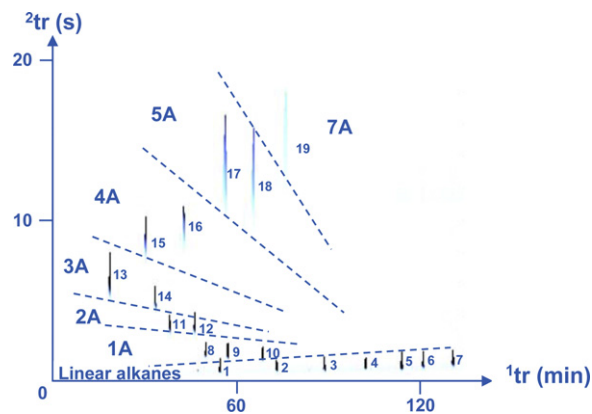


Fig. 2. 2D contour plot of the test mixture (see experimental conditions in Section 2.2).

3.2. 2D experiments

The Fischer Tropsch wax was analyzed by HT-GC×GC in order to check the suitability of the selected columns system and operating conditions for the elution of high boiling point compounds. Linear alkanes of the sample allowed the determination of the heaviest linear alkane eluted thanks to the spiked linear alkane nC_{46} . Fig. 1 shows that linear alkane nC_{68} (641 °C) was successfully eluted under these chromatographic conditions. Branched alkanes and alcohols were also identified. This result shows that increasing the phase ratio of the first column helped eluting higher boiling point alkanes than nC_{60} .

A test mixture of hydrocarbons containing up to seven aromatic rings was also analyzed (Fig. 2): a well-structured chromatogram was obtained without any wrap-around. Compared to Dutriez et al. [11], the increase of the phase ratio used in the second dimension enabled us to elute highly polyaromatic compounds such as coronene in one 20 s modulation period. However, it is obvious in Fig. 2 that compounds containing more than four aromatic rings (*i.e.* compounds labeled 17, 18 and 19) are highly retained in the second dimension leading to a decrease in the interfamily resolution as they are really broad in the second dimension (*i.e.* approximately 6 s wide). Moreover, high boiling point compounds contain numerous or long alkyl chains and are therefore less polar than unsubstituted compounds. Thus, substituted compounds are less retained in the second dimension than their respective parent unsubstituted compound and exhibit less retention difference with saturated compounds. This phenomenon is clearly visible in Fig. 2 in which the possible elution bands of the compounds are indicated.

These new operating conditions provide some exciting possibilities for the analysis of heavy petroleum fractions since compounds with boiling point up to 641 °C will be eluted as well as compounds containing up to seven aromatic rings.

4. Conclusion

HT-GC×GC operating conditions were adapted in order to elute up to 641 °C boiling point alkanes and highly aromatic compounds. Short wide bore columns with a thin film of stationary phase were chosen in order to overcome actual HT-GC×GC limits. Furthermore, an on column injector and a CO₂ cryogenic modulator were used in order to reduce both discrimination and adsorption of high boiling point compounds. Improvements could be expected in order to push even further the boundaries of HT-GC×GC if new polar phases thermally stable at high temperature (above 370 °C) and thinner

film of stationary phase than 0.15 μm for wide bore columns were to be commercialized.

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