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Comparative study of differential flow and cryogenic modulators comprehensive two-dimensional gas chromatography systems for the detailed analysis of light cycle oil

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ABSTRACT

The modulator is the key point of comprehensive two-dimensional gas chromatography (GC×GC). This interface ensures the sampling and transfer of the sample from the first to the second dimension. Many systems based on different principles have been developed. However, to our knowledge, almost only cryogenic modulators are used in the petroleum industry. Nevertheless cryogenic fluids represent some disadvantages in term of safety, cost and time consuming. This paper reports a comparative study between differential flow and cryogenic liquid modulators for the detailed analysis of hydrocarbons in middle distillates type light cycle oil (LCO). Optimization of geometrical dimensions of a set of columns was carried out on the differential flow modulator system in order to reproduce the quality of separation of cryogenic modulation. Then a comparative study was investigated on sensibility and resolution (separation space and peak capacity) between the two systems.

1. Introduction

The complexity of petroleum products such as light cycle oils requires efficient methods of analysis. The molecular information allows a better comprehension of refinery processes and product properties. The comprehensive two-dimensional gas chromatography (GC×GC) is a powerful technique for the molecular characterization of complex samples. The performance of GC×GC for the analysis of petroleum products has been thoroughly documented [1–3]. This technique, which associates two capillary columns coupled together in serial with a modulator at their junction [4,5], provides a large peak capacity to determine the composition of the petroleum cut in saturates, monoaromatic, diaromatic and triaromatic hydrocarbons [3,6,7].

Since the introduction of GC×GC, modulators have been continuously improved. The modulator ensures high sampling rates and sample transfer from the first to the second dimension while respecting Giddings's conservation rules [8]. To guarantee conservation of the first dimension separation achieved, the fraction eluted from the modulator should be no wider than about one-quarter of the 1D peak width [9]. Recommended is the ensurance of at least three to four cuts per peak of the first dimension by the modulator. Thus, a modulation period of 2–8 s is generally chosen [5]. The several different modulators that are commercially available should be classified into two main categories: thermal modulators and valve-based modulators. Thermal modulators are the most frequently used and in turn can be broken down into two categories: those whose principle involves a temperature increase and, inversely, cryogenic modulators. Both modulators have significant disadvantages. In fact, with a heating trap, it is practically impossible to collect volatile compounds. In addition, the final oven temperature has to be 100 °C lower than the upper working temperature of the stationary phase in order to prevent the thermal degradation. In the case of cryogenic modulators, the main disadvantage is the consumption of large amounts of liquid cryogen coolant.

The first diaphragm valve modulator introduced by Bruckner et al. [10], was not as efficient as cryogenic modulation since only 10–20% of sample were redirected in the second dimension. Seeley et al. improved this result with the development of a modulator in which 80% of effluents were sampled [11]. The temperature range is the main drawback of these modulators. Recently, a commercially available Agilent GC×GC system using a differential flow modulator, developed by Seeley et al. in 2006 [12], allows an alternative to the use of liquid cryogen modulator. This new kind of valve modulator is equipped with a fast acting three-way solenoid valve which controls the fill and flush state of the collection channel. This alternating cycle of filling and flushing corresponds to the modulation period. The configuration of this differential flow modulator is simpler and the temperature range is wider than the diaphragm valve modulator. Table 1 summarizes the differ-

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Table 1
Comparison of GC×GC modulators.

Modulator type	Advantages	Drawbacks	References
Thermal	• No liquid cryogen • 100% weight conservation	• Work temperature limit to 230 °C	[4,13–16]
Cryogenic CO_2, N_2	• 100% weight conservation • Peak capacity in second dimension	• Use of liquid cryogen • Bad traping of compounds < C7 (CO_2)	[17–20]
Valve	• No liquid cryogen	• 80% weight conservation • Low modulation period (<2 s) • Work temperature limit to 200 °C	[10,21]
Differential flow	• No liquid cryogen • Modulation of compounds < C7 • Peak capacity in second dimension • 100% weight conservation	• Resolution in second dimension • Use of hydrogen as carrier gas	[11,12]

ent modulators used in GC×GC and presents their advantages and drawbacks.

The aim of this study is to evaluate the performance of the differential flow modulator (Agilent Technologies, Inc., Wilmington, DE) on the detailed analysis of hydrocarbon compounds in light cycle oil (LCO). The optimization of geometrical dimensions of the columns, the flow in each dimension and the fill and flush period were adjusted in order to obtain competitive results when compared with a liquid cryogen modulator. A comparison with the cryogenic modulator in term of separation efficiency and sensitivity is reported.

2. Experimental

2.1. Instrument

In order to compare both modulators, LCO samples were analyzed on a GC×GC-FID Agilent 7890N (Agilent Technologies, Inc., Wilmington, DE) using a differential flow modulator and also on a GC×GC-FID using a Pegasus IVD from Leco Corporation (St Joseph, MI, USA) equipped with a quad jet liquid nitrogen modulator. Table 2 presents the analytical conditions in the two configurations (cryogenic and differential flow modulators) optimized for the comparison (cf. Section 3.1). Detector signals were monitored with Agilent Chemstation software (Agilent) and Chromatof (Leco). The data were converted by GC-Image software (Zoex) for data processing.

2.2. Principle of the differential flow modulator

The differential flow modulator is based on Agilent's capillary flow technology and does not require cryogenics. Fig. 1 illustrates this modulator. The principle of the differential flow modulator was explained elsewhere [12]. Briefly, a three-way solenoid valve receives a controlled supply of typically 19–21 ml/min of hydrogen gas from an auxiliary pressure system. The periodic switching of this three-way valve drives the modulator. The precisely timed and synchronized switching between the *fill* and *flush* states directs discrete sample pulses continuously to the second column. As explained the differential modulator requires high flow in the second dimension which may limit what type of detector can be used. Some adjustments need to be carried out with the SCD detector for example.

3. Results and discussion

3.1. Optimization

According to the literature [11,12], Agilent recommends to use a first dimension of 30 m × 0.25 mm × 0.25 μm coupled with a second dimension of 5 m × 0.25 mm × 0.15 μm involving a flow in the first and the second column of 0.8–1 ml/min and 20–30 ml/min, respectively. The use of such high flow in second dimension leads to high velocity in the column (400–600 cm/s). In this configuration, hydrogen is the best carrier gas thanks to its low viscosity compared to helium and nitrogen [22,23].

The configuration proposed constrains to work at a modulation period of 1.5 s sacrificing the peak capacity in the second dimension. The increase of this modulation time is essential to conserve the interest of the second separation. Increasing modulation time means to increase the fill state of the modulator (collection time). Optimization of the geometrical dimensions is consequently necessary to reproduce separation obtained with cryogenic modulators. The objective of this optimization is to reproduce the LCO separation obtained with a cryogen modulator by using a differential flow modulator. A detailed analysis of middle distillates were carried out by Vendeuvre et al., on 7 s of cryo-modulation with a set of columns of 10 m × 0.2 mm × 0.5 μm–0.8 m × 0.1 mm × 0.1 μm in a "normal phase" separation [3]. The length of first dimension was insufficient to resolve saturates from monoaromatics. In our study a classical set of 30 m × 0.32 mm × 0.25 μm–1 m × 0.1 mm × 0.1 μm was chosen.

With the differential flow modulator, a set of 10 m × 0.1 mm × 0.4 μm–5 m × 0.25 mm × 0.15 μm allows working at a correct modulation time with a sufficient quantity of stationary phase for the separation of interest compounds. The

Table 2
Analytical conditions for the detailed analysis of hydrocarbon compounds in LCO by GC×GC-FID.

	N_2 liquid modulator	Differential flow modulator
Instrument	Pegasus IV Leco	Agilent 7890N
Injector	SSL, 300 °C in split mode (1:400 split ratio), 0.2 μL	SSL, 300 °C in split mode (1:400 split ratio), 0.2 μL
First column	DB-5: 30 m × 0.32 mm × 0.25 μm	DB-5: 10 m × 0.1 mm × 0.4 μm
Second column	BPX-50: 1 m × 0.1 mm × 0.1 μm	BPX-50: 10 m × 0.25 mm × 0.1 μm
Carrier gas	Helium, 1.5 ml/min	Hydrogen, 0.2 ml/min in first dimension, 22 ml/min in second dimension
Oven	40 °C (0.5 min) to 330 °C (10 min) at 1.9 °C/min	40 °C (0.5 min) to 330 °C (10 min) at 1.9 °C/min
Modulator	8 s (hot jet: 0.6 s, cold jet: 3.4 s), +30 °C offset	11 s (10.8 s fill, 0.2 s flush)
Detector FID	100 Hz, 340 °C	100 Hz, 340 °C

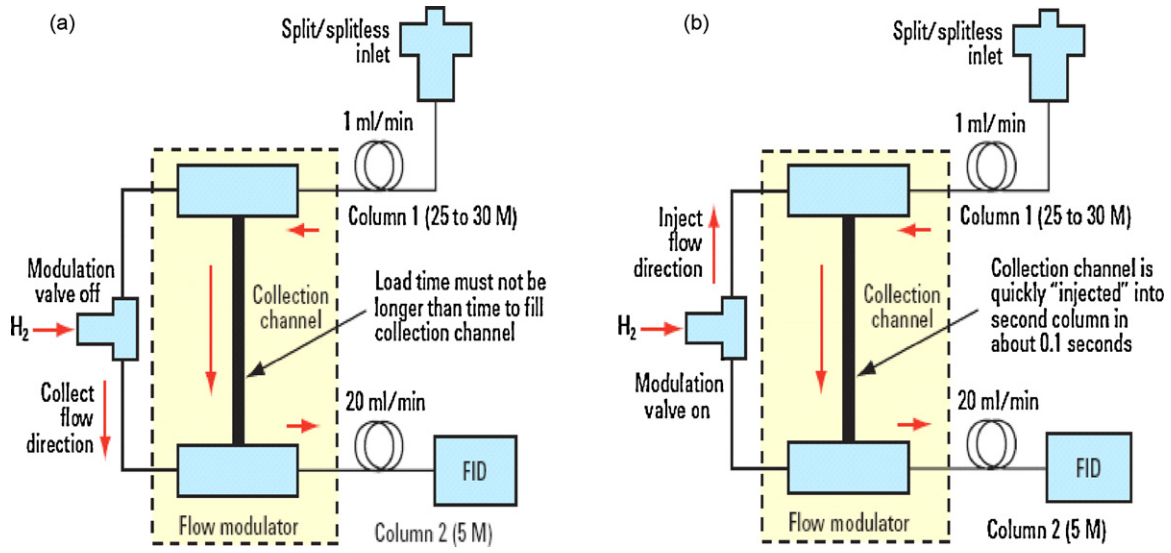

Fig. 1. (a) Flow rates and flow directions during the fill of the collection channel and (b) flow rates and flow directions during the flush of the collection channel (source Agilent).

main drawback of the differential flow modulator is the low resolution in the second dimension compared to the liquid cryogen modulator. To resolve this problem the length of the second column has to be doubled in order to increase the efficiency. The optimized analytical conditions presented in Table 2 allow a detailed analysis of hydrocarbons in 163 min. Fig. 2 presents the LCO detailed analysis obtained with pulse flow modulation configuration after optimization. The separation of saturate, mono-, di-, tri- and tetraaromatic hydrocarbons in five different elution bands achieved is very close to the one obtained in our cryogenic conditions.

3.2. Differential flow vs. cryogenic

3.2.1. Peak width and sensitivity

The peak width in the second dimension is used to describe the resolution and quality of modulation. Second dimension peak widths for volatile and high molecular compounds were thus compared for the two separations. For the molecular weight compounds the peaks in second dimension are wider with the differential flow modulator (0.9–1.1 s compared to 0.7–0.85 s with cryogenic). This difference could be attributed to the focusing effect of the cryogenic modulator which produces narrower peaks than the pulsed

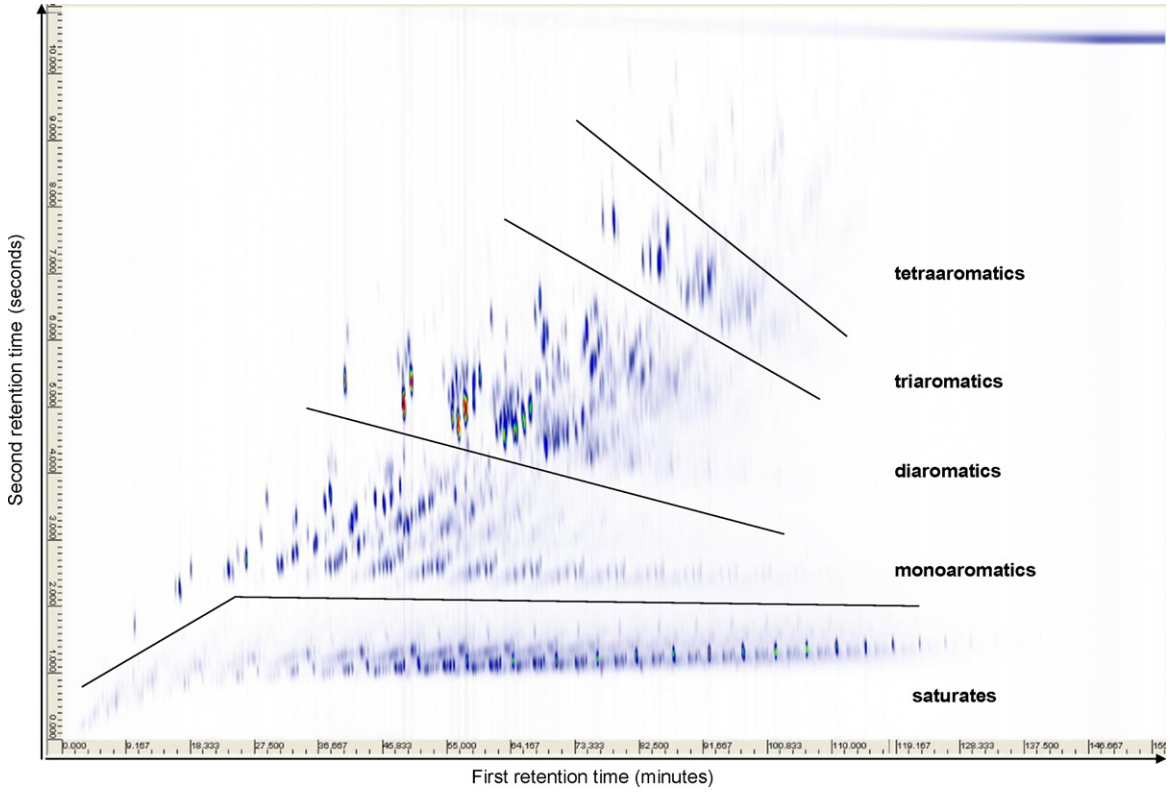

Fig. 2. Detailed analysis of LCO with pulsed flow modulator separation conditions.

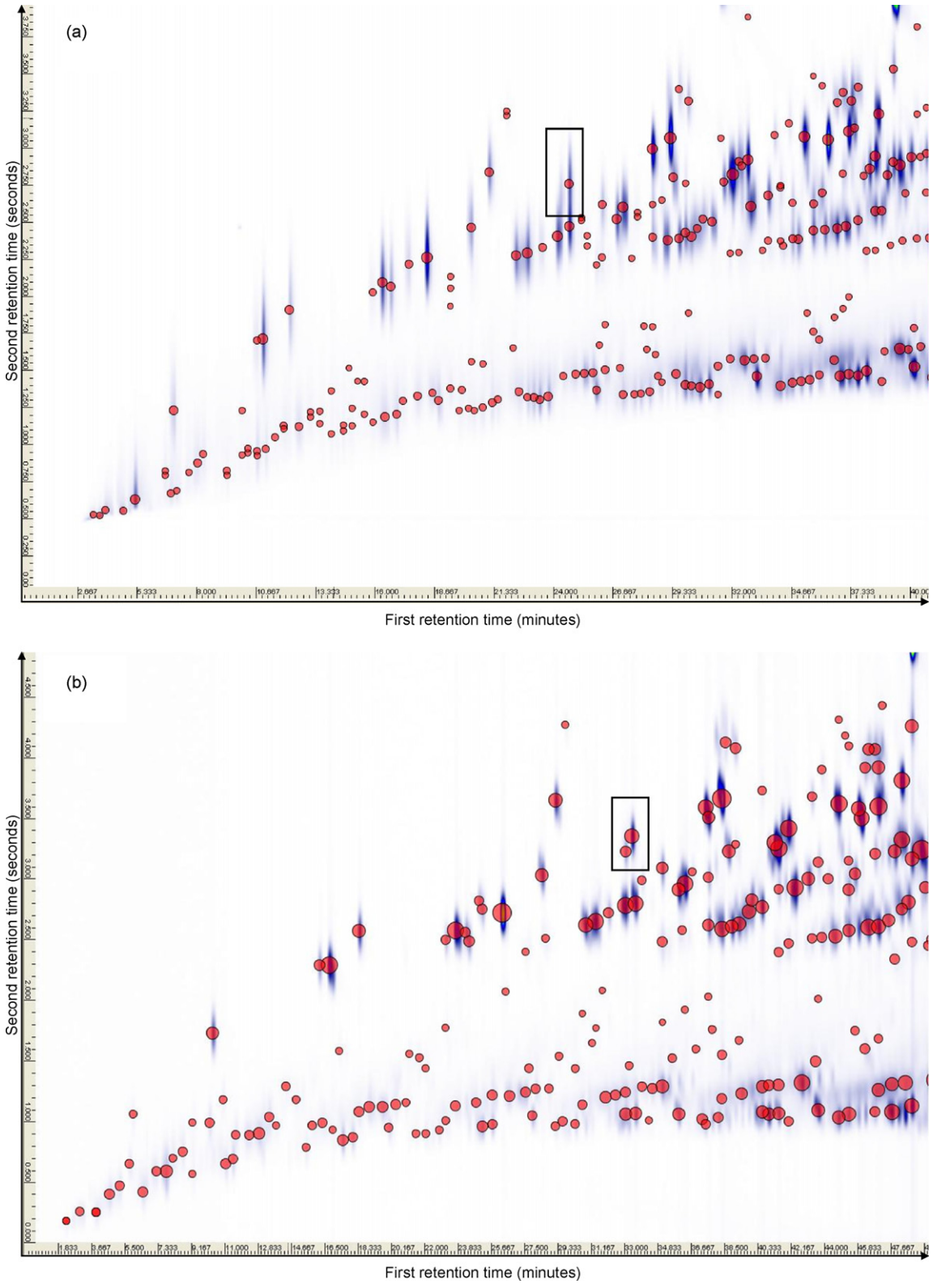

Fig. 3. Zoom on LCO volatile compounds region separation with (a) cryogenic modulation and (b) differential flow modulation.

flow. Signal to noise ratio (S/N) measurements on naphthalene confirmed this observation. In fact a sensitivity gain factor of 2.5 is obtained due to the focusing.

In opposition to this phenomenon, larger peaks in second dimension were observed for volatile compounds with the cryogenic modulation. Fig. 3 shows a zoom on the LCO volatile compounds region for both configurations. With the differential flow modulation, peak widths of 0.4–0.5 s were measured whereas with the cryogenic modulator they were of 0.65–0.7 s. The refocusing of compounds <C10 with liquid cryogen modulator was not as good as with the differential flow modulator. A consequence of this bad focusing is the coelution of two monoaromatics detected as

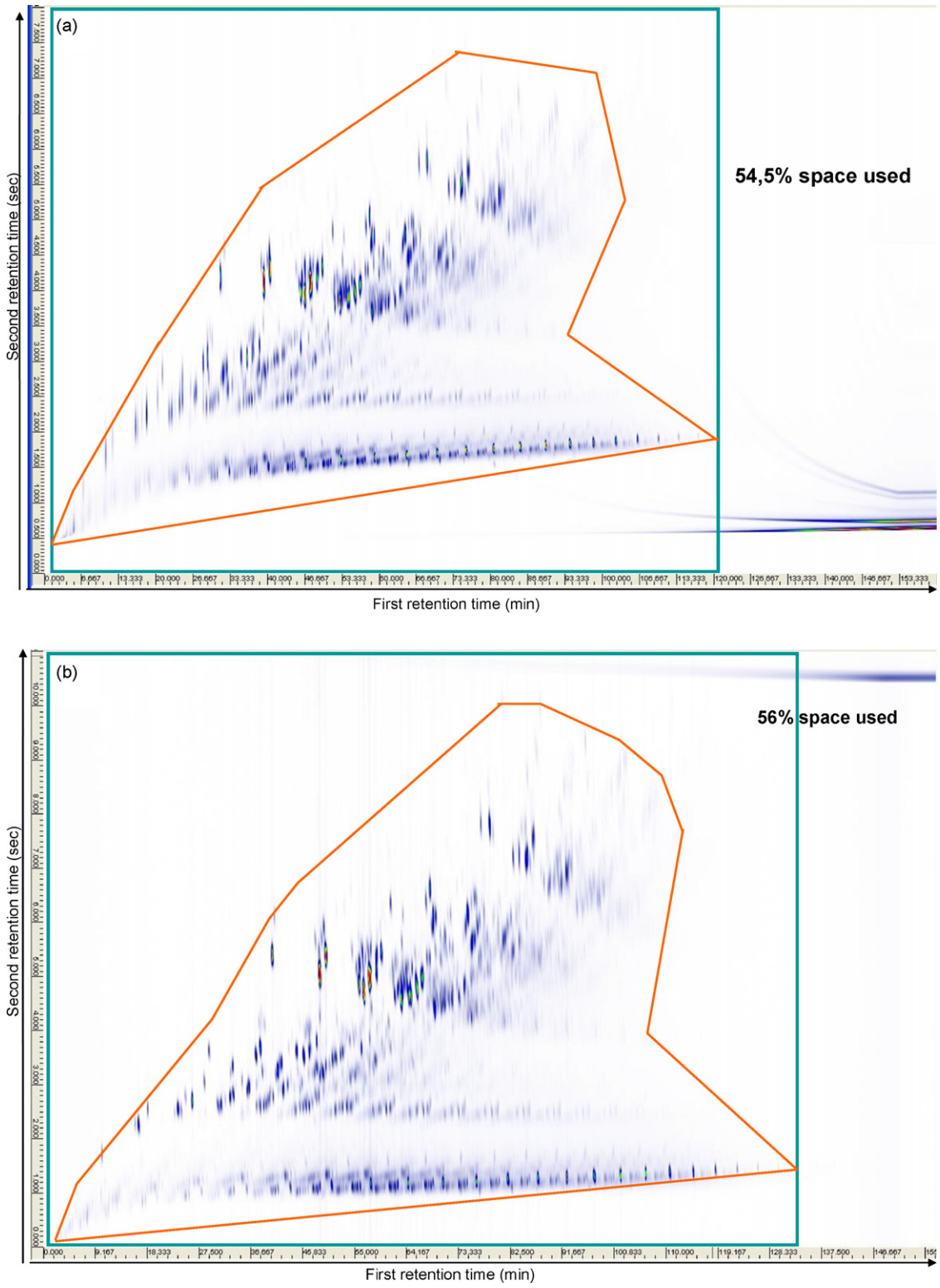

Fig. 4. Chromatograms illustrating the retention space usable (green) and the space used calculated with Delaunay's triangulation algorithms (orange) obtained for the separation of LCO with cryogenic modulation conditions (a) and differential flow modulation conditions (b).

one peak with the cryogenic modulator (Fig. 3, black rectangular). On the separation using differential flow, the good refocusing of the compound gives the necessary resolution to separate the two compounds.

Refocusing issues of volatiles compounds by CO_2 cryogenic modulation has been previously documented [5,16,24]. The temperature of liquid CO_2 is about −70 °C and is insufficient to efficiently trap the most volatile compounds [5]. At the contrary the quad-jet N_2 modulator is able to modulate from C2 to C55 with a reported cold jet temperature as low as −189 °C. However the secondary column chosen in this study (BPX-50) cannot be used below −30 °C. At the beginning of the oven program temperature the com-

Table 3
Peak capacities calculation for the two systems, based on column efficiency (N) and on the retention time of the last eluted compound (t_n) and dead time (t_0) in each dimension.

First dimension	Differential flow	N_2 liquid
$^1t_0$ (s)	40	103
^1tr (s)	351	785
^1k	7.8	6.6
^1w_b (s)	8	10
^1N (plates)	30800	98596
^1N (plates/m)	3080	3287
^1t_n (s)	7620	7980
n_1	231	342
Second dimension	**Differential Flow**	**N_2 liquid**
$^2t_0$ (s)	2.82	0.5
^2t_r (s)	14.2*	4.19
^2k	4.0	7.4
^2w_b (s)	1.08	0.77
^2N (plates)	2766	474
^2N (plates/m)	277	474
^2t_n (s)	14.2	6.96
n_2	22	15
GC×GC system	**Differential flow**	**N_2 liquid**
$n_{GC\times GC}$	5148	5250

pounds release takes more time than with the differential flow not requiring liquid coolant. Even by optimizing the cold and hot jet times and the temperature of the cryo-modulator, the volatiles peaks were still larger than the ones obtained by using the pulsed flow modulator. The solidification of the stationary phase at low temperatures can explain the poor peak width. On the other hand, if the temperature is low enough there will be no migration at all and thus no band broadening. One possibility to avoid this freezing effect could be to use a piece of stationary phase of 100% polydimethylsiloxane in the modulator. The temperature minimum is −60 °C which gives more flexibility.

3.2.2. Separation space

Recently a new model of occupation space was developed for optimizing the operating conditions of GC×GC [25]. This model is a simple tool for the calculation of the percentage of separation space. This convex hull model has been previously used to select column sets and geometrical parameters of secondary columns to analyze target compounds in environmental matrices [25]. The rectangular area of usable space (Fig. 4, green) was calculated using dead time in first dimension ($^1t_0$), retention time (^1t_r) of the last compound eluted and the modulation period. A set of n points distributed in the retention space was considered to define the retention space used. The retention space used was defined by the convex hull which was obtained using the Delaunay triangulation method [26]. The percentage of separation space used was calculated using Eq. (1):

$$\%\ \text{separation space used} = \frac{\text{area of the convex hull}}{\text{area of total retention space usable}} \times 100 \quad (1)$$

Fig. 4 presents a simple picture of the results obtained by the calculation model. Only the apices of the peaks were considered to draw the convex hull of the retention space used and not the peak widths. But as we showed before, the peak widths in the secondary dimension are essentially identical, except for the volatile. This model has been used just to give a first approximation of the quality of separation in the two configurations. The percentage of separation space used was 54.5% and 56% for cryogenic and differential flow modulators, respectively (Fig. 4a and b, orange). The shape of the separation and the results on percentage of separation space used indicate that the quality of separation of the LCO obtained with cryogenic modulation has been reproduced with the differential flow modulator.

3.2.3. Peak capacity

Calculations on the peak capacities of the two systems (presented in Table 2) were also investigated as a comparative tool between the two separations of LCO. The peak capacity of the GC×GC system (nGC×GC) is assumed as equal to the product of the peak capacities in each dimension [27]. The peak capacities in the first (n_1) and second (n_2) dimensions were calculated as follows:

$$n = 1 + \frac{\sqrt{N}}{4} \ln \frac{t_n}{t_0} \quad (2)$$

where N is the column efficiency, t_n and t_0 are the retention time of the last eluted compound and the dead time, for a given dimension, respectively [28]. In practice, the column efficiency in the first dimension was measured at 100 °C on the peak of tridecane (cryogen) and decane (differential flow). Considering that the separation in the second dimension is carried out on isothermal conditions, N_2 was directly obtained from the peak of naphthalene (cryogen) and pyrene (differential flow) in comprehensive LCO separation. In each dimension a retention factor (k) comprised between 4 and 8 was considered for the calculation of column efficiency. Table 3 presents the peak capacities of each dimension and of the GC×GC system for the two configurations tested in this study for the separation of LCO.

The first column efficiency (^1N) measured on the experiment with differential flow modulator is only 30% of the theoretical efficiency for a column of 100 μm of inner diameter. A long modulation time is the consequence of this loss of efficiency in the first dimension. Indeed 11 s of modulation are necessary with the differential flow modulator to reproduce the detailed analysis of hydrocarbons of the LCO and to avoid wrap-around effect. The modulation period and the flows in each dimension are closely linked together. Optimization of one parameter leads to the need for re-optimization of others. In this case, the flow in the first dimension has to be adjusted at 0.2 ml/min with a standard collection channel of 10.8 s fill state and 0.2 s flush state. Thus, this constraint prevents an optimum flow of 0.4 ml/min required for a theoretical efficiency of 100,000 plates. We assume that the efficiency should be better with geometrical dimensions of collection channel adapted for a long modulation time. The plate number for the second column with cryogenic separation is very low compared to about 4000 for such a column. With the cryogenic system the flow in the second dimension is the same and as we chose to work at the optimum of the first dimension, unfortunately we sacrifice the efficiency of the second column.

The plate number of the first column is very low for the differential flow modulator. However, the second column has a very low plate number for the cryogenic modulator. As a consequence the final peak capacities ($n_{GC\times GC}$) are comparable for the two systems. Each configuration needs to be evaluated closely to find the best compromise for the quality of separation.

4. Conclusion

The flow in the first dimension is the essential parameter when using the differential flow modulator as it influences all the other parameters of the separation (dimensions of columns, modulation time). In this study, a configuration allowing a good separation of LCO was found in adjusting the dimensions of the column for a low flow in the first dimension.The differential flow modulator (Agilent Technologies, Inc., Wilmington, DE) represents an alternative because it does not require cryogenic fluid. With an optimized configuration of columns and suitable flows, it is possible to match the performance of cryogenic modulators in terms of resolution and

peak capacity. This solution enables easier the use of GC×GC for routine analysis.

When the sensitivity is the analytical challenge, GC×GC users may prefer the gain factor of the focusing to target traces of compounds in complex matrices for example. Indeed, the choice of modulator will have to depend on the specific application. Introducing the second carrier gas flow, the differential flow modulator allows considering other experimental conditions much easier than with the cryogenic modulator. On the other hand, the cryogenic modulator is more flexible to convert the GC×GC to conventional GC method, just in turn-off the modulation unit.

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