

Multidimensional gas chromatography for the detailed PIONA analysis of heavy naphtha: Hyphenation of an olefin trap to comprehensive two-dimensional gas chromatography

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Abstract

A multidimensional method providing the composition of a heavy naphtha in paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) in the C₈–C₁₄ range is presented. The analytical set-up consists in a silver modified silica olefin trap on-line coupled to comprehensive two-dimensional gas chromatography (GC × GC). In this configuration, hydrocarbons are separated, in gaseous state, in two fractions, saturate and unsaturate, each fraction being subsequently analysed by GC or by GC × GC. The resolution between saturates and olefins was found to be improved compared to a single GC × GC run. The characterisation of the olefin trap highlights the benefits and the limits related to the use of that stationary phase as a double bond selective fractionation medium.

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1. Introduction

The detailed analysis of petroleum cuts is required for refinery processes monitoring and for product specifications. Two gas chromatographic (GC) techniques, providing different levels of detail, have been normalised to obtain the chemical composition of commercial gasoline (boiling up to 200 °C) [1,2]. The first one is to achieve a high resolute GC separation that provides individual components analysis with an identification based on retention indices [1]. The second possibility, widely used in refineries, is a multidimensional method (PIONA analyser) based on the separation of each different constituting chemical group (alkanes or paraffins, isoalkanes or isoparaffins, alkenes or olefins, cycloalkanes

or naphthenes, aromatics) in a dedicated column or trap [2]. Since the introduction of the PNA analyser in 1971 [3] to determine the content of paraffins, naphthenes and aromatics for each carbon atoms through C₁₀ by sequential separations on polar, non-polar and 13 × molecular sieve columns, the system has evolved to extend the analysis to olefins using an olefin trap [4] and to isoparaffins using a 5A molecular sieve column. However, these techniques are limited when analysing refinery cuts having a higher boiling range, such as heavy naphtha (C₈–C₁₄). Using high resolution GC, significant coelution may indeed occur above C₁₀, especially if blending cuts derived from fluid catalytic cracking (FCC) – olefinic naphtha – are analysed, because the high number of components is not compatible with the peak capacity of the GC column. The limitation of the PIONA analyser is related to the maximum number of carbon atoms (C₁₀) of molecules to be handled, principally owing to the high

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temperature required to elute hydrocarbons from the molecular sieves. Thus, both methods fail to provide the detailed or group-type analysis of heavy naphtha in the C₈–C₁₄ range.

One major advance in gas chromatography techniques was the introduction of comprehensive two-dimensional gas chromatography (GC × GC) giving a greater peak capacity than conventional GC [5]. For a recent and exhaustive overview of this technique, its instrumentation and applications, the reader is referred to [6]. One interesting feature of GC × GC applied to petroleum samples is the combination of two independent separation mechanisms according to the volatility in one dimension, and to the polarity in the other dimension; hence the boiling range and the chemical group distribution can be simultaneously obtained. However, the selectivity of the second dimension remains sometimes insufficient for the PIONA analysis with a carbon atom breakdown. For instance, the separation between naphthenes and olefins can not be achieved in complex samples containing all chemical families, even using GC × GC–TOF–MS because fragmentation of these compounds can produce the same ions at low resolution.

In order to improve the detailed PIONA analysis of a heavy naphtha, a multidimensional approach is proposed. It is based on the fractionation by an olefin trap of the saturate and unsaturate fractions of a petroleum cut followed by the GC × GC analysis of each fraction. The implementation of an olefin trap hyphenated to GC capillary columns is presented. The selectivity and the capacity of the trap are evaluated and the possibility to extend the analysis to heavier hydrocarbons is studied. The last part of the paper focuses on the hyphenation of the olefin trap to GC × GC for an application to a complex heavy naphtha.

2. Experimental

2.1. Retention and selectivity measurements in the olefin trap

A commercial olefin trap was purchased at Analytical Controls (Rotterdam, The Netherlands). It was installed in the oven of a HP5890 chromatograph (Agilent Technologies, Massy, France). Helium was the carrier gas at a flow rate of 15 ml/min. A volume of 0.1 μl of hydrocarbons diluted at 0.5% (w/w) in pentane was injected in the packed-column inlet heated at 250 °C. Detection was achieved by a flame ionisation detector set at 280 °C.

For evaluation of the effect of silica impregnation with silver ions, bare silica (130 m²/g, 40 μm) obtained from Merck (Darmstadt, Germany) was used. Two columns were made with inox tubing (length: 30 cm, diameter: 1/8 in.): one was filled with silica and the other with silica impregnated with 5% (w/w) silver nitrate (Sigma Aldrich, Lyon, France). The silver silica was prepared according to the description given in [7].

2.2. Hyphenation between the olefin trap and GC capillary columns

The olefin trap was used to fractionate the saturated and the unsaturated hydrocarbons of a synthetic mixture. Then, the two fractions were successively analysed by GC or GC × GC. The analytical scheme is depicted in Fig. 1 and the different items are labelled (#) in the following description. In order to control the two separation steps independently, the olefin trap (#3) was installed in a first chromatograph (HP5890, #1) and the set of capillary columns used for GC × GC (#10–11) was placed in a second chromatograph (HP6890, #2). Helium was provided to the injector (#5) of the first chromatograph by the auxiliary channel (Electronic Pressure Control, #6) of the second chromatograph to ensure a constant pressure during the analysis (150 kPa).

Two six-ways valves (Valco) were installed in a heated block (#4) in the first chromatograph to enable the backflush and/or isolation of the trap. The olefin trap was connected to the valve 1 (V1) that was configured to by-pass the trap in off position. The foreflush/backflush modes were obtained by acting the valve 2 (V2). The three configurations corresponding to foreflush elution (V1 on/V2 off), backflush elution (V1 on/V2 on) from the olefin trap and isolation of the olefin trap (V1 off/V2 off) are shown in Fig. 1. An insulated transfer line went through the oven walls of the chromatographs to connect the olefin trap to the GC columns. The effluent from the first chromatograph was split at a tee connection located in the second chromatograph. From one side of the tee, a deactivated fused silica tubing (50 cm × 0.32 mm i.d.) (Chrompack, Les Ulis, France) (#12) was placed before the set of GC × GC columns consisting in a 10 m-long PONA (Agilent Technologies) column (0.2 mm i.d.; 0.5 μm) (#10) connected to a 0.8 m-long BPX50 (SGE, Courtaboeuf, France) column (0.1 mm i.d.; 0.1 μm) (#11). From the other side of the tee, a retention gap of deactivated fused silica tubing (#12) acted as a pressure drop (250 cm × 0.32 mm i.d.) to split the flow and to reduce the quantity of analytes injected in the capillary columns. Two FIDs set at a temperature of 300 °C were used to monitor the signal from the GC(×GC) separation (FID A, #8) and from the olefin trap (FID B, #9). The separation in capillary columns could be performed either in a non-modulated mode (GC–GC) or in a modulated mode (GC × GC) using a homemade dual CO₂ jets modulator (#7) whose description is given elsewhere [8] and which is available at Thermo (Milan, Italy).

2.3. Chemicals

All chemicals used in this study are hydrocarbons available at Sigma–Aldrich. Analytical gases were provided by Air Liquide (Feyzin, France) at a purity of minimum 99.999%.

A naphtha cut and a FCC cut were provided by IFP development units.

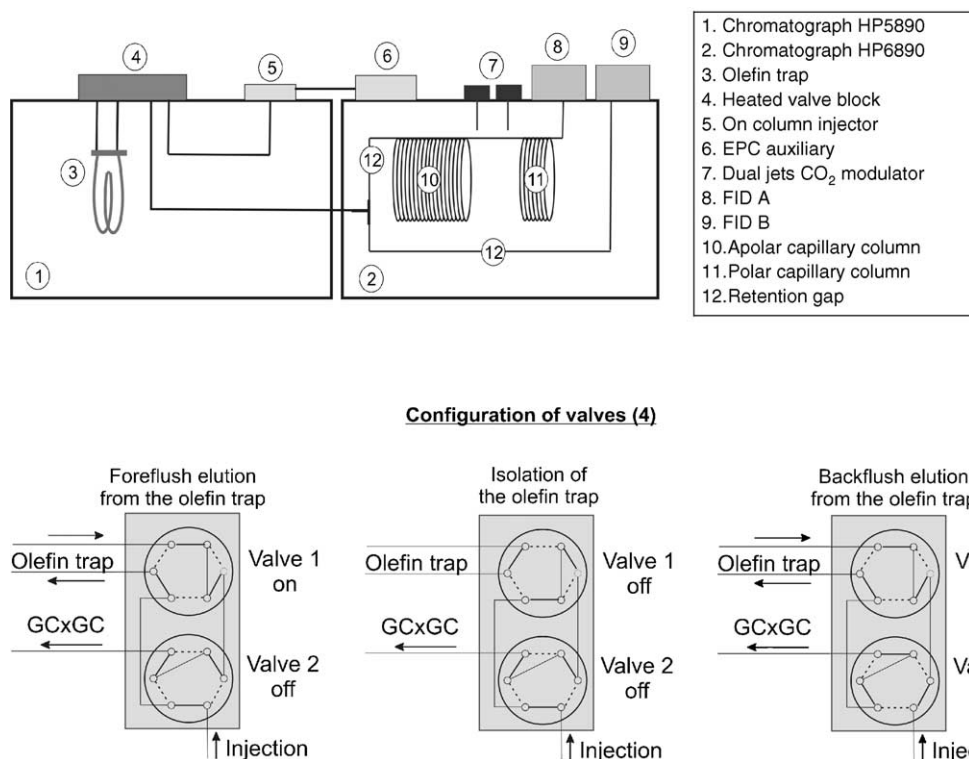


Fig. 1. Schematics of GC × GC–olefin trap hyphenation where the configurations of valves corresponding to different elution modes are detailed.

3. Results and discussion

3.1. Trapping efficiency of a silver silica column for the selective separation of olefins from saturates in the C₈–C₁₄ range

A commercial olefin trap, containing a stationary phase composed of silica (80–120 mesh) modified with silver (8%, w/w), was chosen to perform the separation of saturates and olefins. Hydrocarbons having a double bond display a high affinity towards silver via reversible charge transfer mechanisms [9]. Saturate compounds (naphthenes and paraffins) are eluted at a relatively low temperature, while olefins can be eluted by heating the trap [4]. In a first approach, the olefin trap was used as a GC column to determine its selectivity towards paraffins and olefins (see Section 2.1). Octene-1 was eluted after *n*-pentadecane and the selectivity between these two compounds was found to increase from 2.1 to 4.3 when decreasing the temperature from 240 to 200 °C. The selectivity, also expressed as a difference of the Kovats indices between an olefin and a paraffin having the same number of carbon atoms, was higher than 700, and corresponds to a difference of seven carbon atoms. The high selectivity of the trap towards olefins can be confirmed through thermodynamic considerations.

Thermodynamics of a GC separation allow to relate the partition coefficient (*K*) of a solute between the gas phase and the stationary phase to the enthalpy of interaction (ΔH)

towards the stationary phase by:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

Since the entropic term (ΔS) is assumed to be constant, and the retention factor (*k*) can be obtained from the partition coefficient and the phase ratio, the relation can be re-written as follows, where *C* is constant:

$$\ln k = -\frac{\Delta H}{RT} + C \quad (2)$$

The retention factors (*k*) of test compounds from paraffin, olefin and naphthene groups were measured at different temperatures between 120 and 240 °C. The operating temperature range was chosen to enable sufficient volatility of compounds and to respect the maximum temperature upper limit of the trap advocated by the manufacturer. In Table 1 are reported the retention factors measured for all the test compounds, and the enthalpy of interaction determined from the slope of curves obtained by plotting the logarithm of the retention factor against the reciprocal of temperature (correlation factors were found greater than 0.99). Results reported in Table 1 show that the interaction of paraffins increases with the number of carbon atoms, with a mean contribution of about -5.7 kJ/mol per carbon atom. As a comparison, Kiselev and Yashin [10] also demonstrated a linear relationship between the enthalpy and the number of carbon atoms on silica, with a similar contribution of a methyl group (-4.4 kJ/mol). The retention of naphthenes was similar to that

Table 1

Retention factors (k') and enthalpy interaction (ΔH) values obtained for paraffins (P), naphthene (N) and olefins (O) in the olefin trap for different level of oven temperature (T)

	k'	T (°C)								$-\Delta H$ (kJ/mol)	
		120	140	160	180	200	210	220	230		240
P	Octane	16.71	8.09	4.10	2.60	nd	nd	nd	nd	nd	49.9
	Nonane	35.1	15.17	7.34	4.29	nd	nd	nd	nd	nd	54.2
	Decane	75.83	29.24	12.79	6.57	nd	nd	nd	nd	nd	61.8
	Undecane	141.19	57.17	22.63	10.66	nd	nd	nd	nd	nd	65.0
	Dodecane	ne	114.12	40.97	17.63	7.66	nd	nd	nd	nd	73.3
	Tridecane	ne	212.49	71.15	28.47	11.66	nd	nd	nd	nd	78.6
	Tetradecane	ne	ne	141.44	48.50	21.19	14.14	9.96	6.51	4.48	80.4
	Pentadecane	ne	ne	ne	85.55	32.06	21.34	15.55	10.02	7.1	82.5
N	Tertbutyl-Cyclohexane	47.41	20.09	9.83	5.31	nd	nd	nd	nd	nd	53.9
	Hexane	ne	ne	ne	ne	23.44	14.20	9.26	5.91	nd	93.6
O	Octane	ne	ne	ne	ne	138.50	76.92	42.5	24.02	15.27	106.3
	Nonene	ne	ne	ne	ne	ne	174.28	100.39	55.73	32.45	115.7
	Undecene	ne	ne	ne	ne	ne	ne	ne	134.40	77.15	119.0

nd: not determined; ne: not eluted in acceptable analysis time.

of paraffins, the interaction enthalpy of tertbutylcyclohexane (53.9 kJ/mol) being close to that of *n*-decane (61.8 kJ/mol). The interaction of olefins towards the stationary phase also increases with the number of carbon atoms but the enthalpy of an olefin is at least 54 kJ/mol higher than that of a paraffin having the same number of carbon atoms. In the complexation reaction between olefin and silver ion, the stability constant K_1 of the complex can be related to the two partition coefficients K_L and K_L^* by the Eq. (3) [11]:

$$K_L = K_L^*(1 + K_1[Ag^+]) \quad (3)$$

The partition coefficient K_L was determined from the retention volume of the olefin in silver nitrate–ethylene glycol stationary phase, and K_L^* from the retention in ethylene glycol alone. This relationship can be transposed to the case of a stationary phase of silver silica. Thus, two different contributions are highlighted in the interaction of olefins towards this stationary phase: non-specific adsorption on silica, depending on the number of carbon atoms, and specific adsorption on the silver sites, depending on the silver content. The determination of specific interactions (K_1) between olefin and silver assumes that data can be obtained with the stationary phase alone (K_L^*). As the silica used in the olefin trap was not available, two columns were filled with silica and with silica impregnated with 5% silver. The interaction enthalpy of octane and octene-1 were, respectively, 39.8 and 44.2 kJ/mol for silica and 40.7 and 74.2 kJ/mol for silver silica. These results show (i) the difference of ΔH between olefins and paraffins is higher when using silver silica (33.5 against 4.4 kJ/mol) which reveals specific interaction between olefins and silver; (ii) ΔH values reported here are lower than those obtained with the olefin trap (74.2 kJ/mol versus 106.3 kJ/mol for octene) owing to less adsorption probably resulting from a lower specific area and to weaker specific interaction (lower content of silver).

The retention of olefins heavier than undecene was too high in the operating temperature range and could not be studied. Obviously, the strong retention of heavy olefins in the trap is a drawback for the analysis of hydrocarbons in the C_8 – C_{14} range. Results of Table 1 show that the interaction enthalpy of the heaviest paraffin (*n*-pentadecane, 82.5 kJ/mol) is lower than the lighter olefin (hexene-1, 93.6 kJ/mol) indicating, from a thermodynamic point of view, the ability of the olefin trap to separate olefins from paraffins in the C_8 – C_{14} range provided suitable elution conditions of heavy olefins from the trap can be found. The olefin trap will be used to separate olefins from paraffins under binary conditions indicated as “trapping” and “desorption” steps; although misleading, these terms should be considered as “strong retention” and “elution (at higher temperature)”.

3.2. Operating considerations for the separation of olefins using hyphenation between the olefin trap and GC

The silver silica trap was not designed for direct coupling with capillary GC: as it is a 1/8 in. column, this involves some constraints regarding the flow and the loadability. First, the effluent from the trap was split using a tee connection to reduce the flow and the injected quantity in the GC columns. In Section 3.6, the influence of the split on the quantitative response will be evaluated. Secondly, in order to better focus olefins prior to their introduction in the analytical columns, and then reduce the peak volume, the trap was backflushed for desorbing the olefins. One other advantage is the reduction of the analysis time, especially for heavy olefins.

Chromatograms of Fig. 2 show the desorption (at 240 °C) in the foreflush or in the backflush modes of octene-1, decene-1, dodecene-1 and tetradecene-1 after their trapping in the olefin trap (at 180 °C, 15 min). The trapping temperature is a compromise for fast elution of paraffins without breakthrough of olefins (as pointed out previously, the selectivity

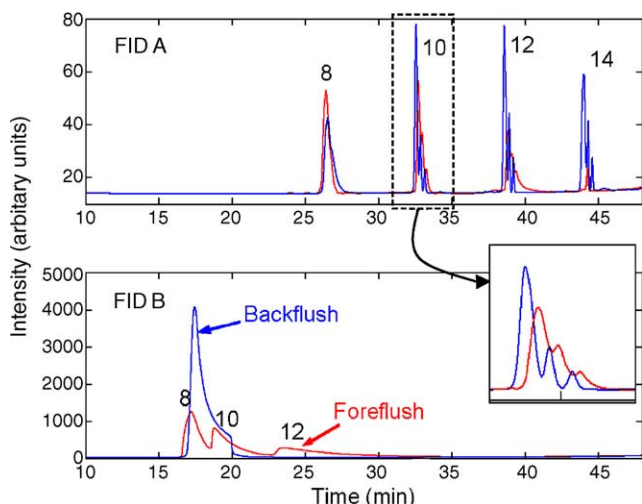


Fig. 2. Chromatograms of an olefin test mix composed of octene-1 (8), decene-1 (10), dodecene-1 (12), tetradecene-1 (14) after adsorption and desorption from the olefin trap. Upper: FID A signal obtained after GC separation of the effluent from the trap; Lower: FID B signal monitoring the effluent from the trap. Conditions: oven #1: $T = 180^{\circ}\text{C}$ (15 min) + $30^{\circ}\text{C}/\text{min} \rightarrow 240^{\circ}\text{C}$ (20 min); oven #2: $T = 30^{\circ}\text{C}$ (15 min) + $5^{\circ}\text{C}/\text{min} \rightarrow 200^{\circ}\text{C}$, $P = 150$ kPa; valve configuration: red foreflush mode: V1 on, V2 off; blue backflush mode: V1 on; V2 off (0–15 min), on (15–30 min).

between paraffins and olefins decreases when the temperature increases). Under these conditions, all paraffins in the C_8 – C_{14} range were eluted in less than 15 min, which enables the choice of the appropriate trapping time. The effluent from the olefin trap was recorded by FID B after transit in the deactivated fused silica tubing in the second chromatograph. As expected, peak tailing and retention of olefins observed in the foreflush mode were limited in the backflush mode. For instance, dodecene-1 is eluted in about 20 min at 240°C and tetradecene-1 is only partially eluted from the olefin trap after 40 min in the foreflush mode whereas the full desorption of all olefins in the backflush mode only lasts 3 min. Thus, the backflush allows reducing the transfer volume between the trap and the GC columns by a factor 8 for olefins from C_8 through C_{12} . The GC–GC separation is monitored by FID A. After their desorption from the olefin trap, solute focusing is performed at 30°C in the deactivated fused silica tubing; as the oven temperature raises for GC separation, their vapour pressure increases for subsequent introduction in the GC–GC columns [12]. The efficiency of the retention gap is demonstrated on the shape of solvent peak as its width (measured at 1% of its height) was only 0.35 min with the retention gap while it was 1.2 min without.

3.3. Isomerisation

Unlike the low-resolution separation monitored by FID B, the chromatogram obtained from FID A connected to the capillary columns offered far more theoretical plates and highlighted an unexpected phenomenon, whatever the flush mode used: more than the four expected peaks of octene-1,

decene-1, dodecene-1 and tetradecene-1 were present in the chromatogram and isomerisation of olefins in the trap was assumed. As already shown by Buchanan and Nicholas [13], significant isomerisation from normal to branched olefins was reported to occur in the trap (4–23% for C_6 – C_{10}). Silica can exhibit acidic properties if it is not deactivated [14] and acts as an acidic catalyst for isomerisation of olefins by migration of a pair of electrons together with either hydrogen or an alkyl group. The former rearrangement results in a double bond shift; the latter in skeletal recombination. As systems implementing the olefin trap for the separation between olefins and saturates often use a hydrogenation step, isomerisation by a shift of the double bond cannot be evidenced. When the trap was by-passed, only one peak per olefin was detected.

In order to investigate the role of silver, the trap was replaced by a tube having the same dimensions and filled with unmodified bare silica heated at 240°C to enable similar separation process to be performed except the composition of the trapping material. Different isomers of linear octene (octene-1, trans-octene-2, trans-octene-3, trans-octene-4) were injected separately (Fig. 3). As found using the silver silica trap, several extra peaks were detected near the main peak; some of them could be identified by comparing their retention time to that of reference isomers, confirming the double bond shift. The proton affinity of alkylcarbonium ions indicates the preferred formation of secondary versus normal ions by margins of 15–25 kJ/mol depending on the number of carbon atoms [15]. An increase of temperature from 150 to 240°C results in a decrease of about 15–20% of the area percent of the main isomer (Table 2): obviously, the high temperatures used for trapping and desorption steps is a severe drawback if one wants to avoid isomerisation. These results could not be obtained in the case of silver silica

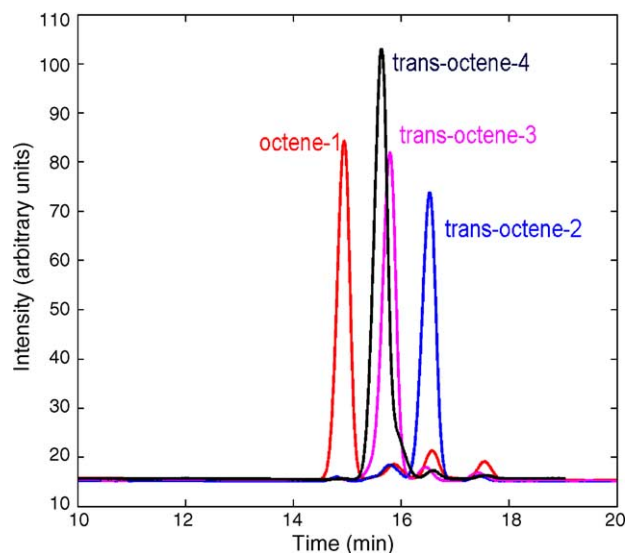


Fig. 3. Overlay of chromatograms obtained after injection of octene-1 (red), trans-octene-2 (blue), trans-octene-3 (pink), trans-octene-4 (black). Oven #1 – ($30\text{ cm} \times 1/8$ in.) – column filled with silica. $T = 240^{\circ}\text{C}$; oven #2: $T = 50^{\circ}\text{C}$. Valve configuration: V1 on; V2 off.

Table 2
Influence of the trapping temperature (oven #1) on the area of desorbed peak for octene-1, decene-1 or dodecene-1

Area (%)	150 °C	180 °C	240 °C
Octene-1	93	88.4	81.3
Decene-1	85.3	79.2	71.2
Dodecene-1	76	68	62.5

Conditions: (30 cm × 1/8 in.)-column filled with silica. Oven #2: $T = 50\text{ }^{\circ}\text{C}$. Valve configuration: V1 on; V2 off.

since the retention in the trap was too high to evaluate the influence of temperature. However, similar phenomena can be assumed in the olefin trap as the ratio of peaks detected after isomerisation of olefins in the olefin trap and in the silica column was similar: for the group of peaks related to decene, the area percents were, respectively, 74.9/17.8/7.3 and 71.2/19.7/8.9. Isomerisation in the trap will inevitably involve identification and quantification problems if the characterisation of individual isomers is wanted.

3.4. Capacity of the olefin trap

The capacity of the trap is of major importance to avoid breakthrough of olefins during the trapping. It was evaluated by injecting $0.4\text{ }\mu\text{l}$ of solutions of octene-1 in pentane having a concentration in the range 0.062–36.5% (w/w). Results given in Fig. 4 show the areas measured in the foreflush step (trapping of the olefin) and in the backflush step (desorption of the olefins). For a correct quantification, the areas of octene-1 and related isomers formed in olefin trap were summed-up. At low concentrations, the relationship between the ‘backflush’ area and the injected quantity of olefin is linear and no breakthrough occurs during the foreflush step (insertion of Fig. 4). Above 40 nmol, the trap has reached its maximum capacity: the backflush area remains constant whereas the ‘foreflush’ area increases linearly as break-

through occurs. A linear relationship ($y = 44026x - 6.57$, $R^2 = 0.9983$) is obtained between the injected quantities (x , μmol) and the sum of areas (y , pA s) of peaks eluted in the foreflush step (untrapped analytes) and in the backflush step (trapped analytes), which demonstrates the linearity of the detector and the total recovery of analytes, whether the trap is saturated or not. The breakthrough of olefins corresponds to a very low injected quantity (equivalent to 40 nmol of octene or to a content of 1.8% (w/w) in a volume of $0.4\text{ }\mu\text{l}$) indicating that the number of sites available for complexation with silver is restricted. If necessary, the total olefinic content should be adjusted at 1.8% (w/w) by dilution of the sample.

3.5. GC × GC analysis of a synthetic hydrocarbon mix

Before dealing with the real samples, the behaviour of aromatic hydrocarbons in the trap was investigated to evaluate (i) their reversible adsorption and (ii) their retention compared to olefins. Ethylbenzene, isobutylbenzene and naphthalene used as test compounds show correct trapping at $180\text{ }^{\circ}\text{C}$ (no breakthrough) and desorption at $240\text{ }^{\circ}\text{C}$ (conditions of Fig. 2) indicating the behaviour of aromatic and diaromatic hydrocarbons in the trap is similar to that of olefins.

A complete hydrocarbon mix, representative of all hydrocarbon families in the $\text{C}_8\text{--C}_{14}$ range, was subjected to the olefin trap–GC × GC separation (Fig. 5). Detailed operating conditions are reported in Table 3. Saturates were eluted from the trap in 15 min at $180\text{ }^{\circ}\text{C}$ while unsaturates were trapped. The trap was isolated to allow the GC × GC separation of saturates. After the elution of saturates is completed and the oven had cooled down to the initial temperature of the program, desorption of unsaturates is performed by heating the trap to $240\text{ }^{\circ}\text{C}$ before switching the valve 1 in order to enable backflush desorption. GC × GC conditions were the same for saturate and unsaturate hydrocarbons. The multidimensional

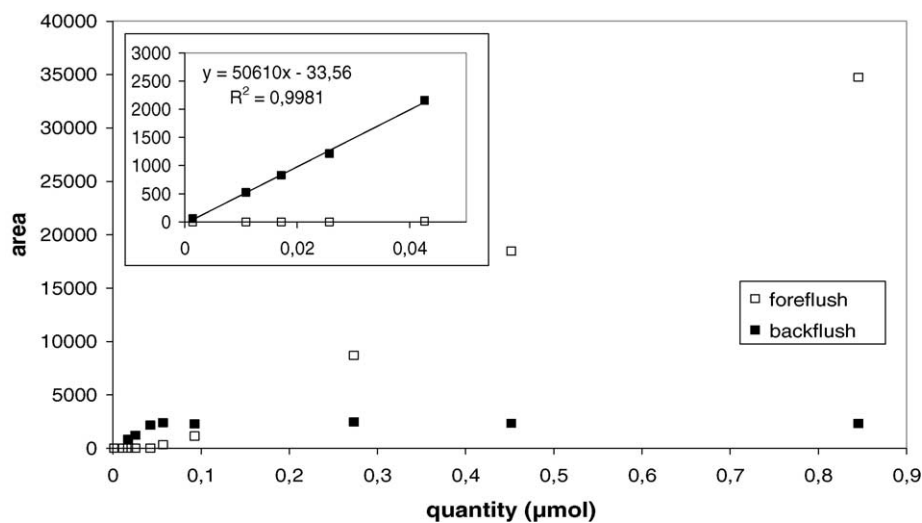


Fig. 4. Plot of the area of octene-1 in the foreflush step (trapping) and in the backflush step (desorption) vs. injected quantity. A zoom at low concentrations is given in the insert. Conditions: oven #1: $T = 180\text{ }^{\circ}\text{C}$ (15 min) + $30\text{ }^{\circ}\text{C}/\text{min} \rightarrow 240\text{ }^{\circ}\text{C}$ (20 min); oven #2: $T = 30\text{ }^{\circ}\text{C}$ (15 min) + $5\text{ }^{\circ}\text{C}/\text{min} \rightarrow 200\text{ }^{\circ}\text{C}$, $P = 150\text{ kPa}$; valve configuration: V1 on; V2 off (0–15 min), on (15–30 min).

Table 3
Operating conditions for the olefin trap–GC × GC separation of a hydrocarbon mix

Temperature oven #1 trap	180 °C (60 min) + 30 °C/min → 240 °C (20 min)	
Temperature oven #2 GC × GC	0 °C (15 min) + 5 °C/min → 200 °C + 30 °C/min → 30 °C (5 min) + 5 °C/min → 200 °C	
Pressure	150 kPa	
Modulation	10–50 min then 70–90 min (4 s period)	
Time	Valves sequence	
	V1	V2
0–15	On	Off
15–60	Off	Off
60–62	Off	On
62–90	On	On

separation according to the unsaturation degree (olefin trap), volatility (first apolar column) and polarity (second polar column) allows to separate hydrocarbons in four groups: paraffins and naphthenes, olefins and aromatics. Within each group, a subdivision according to the number of carbon atoms is possible. One should keep in mind that a detailed analysis based on the position of the double bond will not be possible owing to the isomerisation in the trap.

As the modulation was stopped during the equilibration time between the two GC × GC separations of saturate and unsaturate hydrocarbons to avoid useless consumption of CO₂, modulation sequences of the two GC × GC runs are not synchronised. This means that the location in the second dimension of bands of saturates can not be directly compared to that of unsaturates. A modification of the program driving the CO₂ valves should allow several synchronised sequences of modulation in one analytical run.

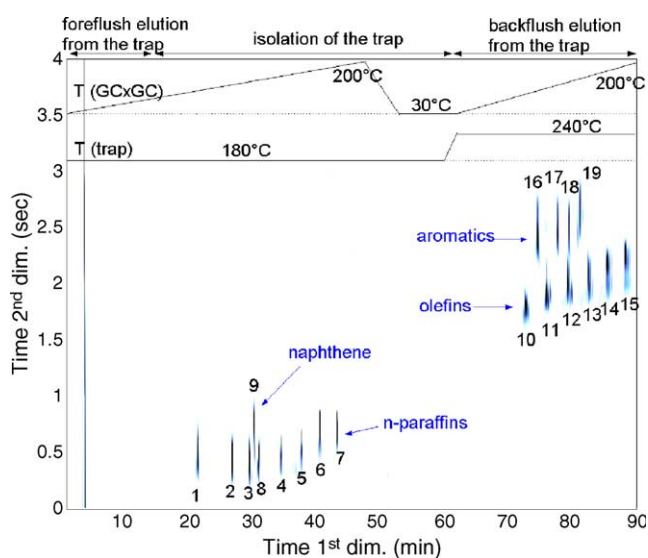


Fig. 5. GC × GC chromatogram of unsaturate and saturate fractions of an hydrocarbon mix: *n*-octane (1), *n*-nonane (2), *n*-decane (3), *n*-undecane (4), *n*-dodecane (5), *n*-tridecane (6), *n*-tetradecane (7), 4-methylnonane (8), tertbutylcyclohexane (9), octene-1 (10), nonene-1 (11), decene-1 (12), undecene-1 (13), dodecene-1 (14), tridecene-1 (15), ethylbenzene (16), *n*-propylbenzene (17), isobutylbenzene (18), 1,4-diethylbenzene (19). Conditions: see Table 3.

3.6. Recovery

Quantitative analysis requires the determination of recovery of hydrocarbons from the olefin trap and the evaluation of the split occurring after the olefin trap.

The influence of changes of temperature on the split ratio during the analysis is discussed from relationships established using theoretical considerations that can be found elsewhere [16]. The local velocity u of a fluid of viscosity η through a capillary column of radius r satisfies the Darcy law:

$$u = -\frac{r^2}{8\eta} \frac{dp}{dz} \quad (4)$$

where p is the pressure and z the ordinate along the column length. It is assumed that the fluid is an ideal gas, i.e.

$$pu = p_i u_i = p_o u_o \quad (5)$$

where the subscripts i and o refer to inlet and outlet of the column.

Combining Eqs. (4) and (5), the velocities at the column inlet and outlet are given by:

$$u_i = \frac{r^2}{16\eta L} \frac{(p_i^2 - p_o^2)}{p_i} \quad (6)$$

$$u_o = \frac{r^2}{16\eta L} \frac{(p_i^2 - p_o^2)}{p_o} \quad (7)$$

The following notations are used to write these equations for the first GC × GC column ($x=1$), the second GC × GC column ($x=2$), and the retention gap ($x=3$): L_x , length of column x ; r_x , radius of column x ; $p_{i,x}$, inlet pressure of column x ; $p_{o,x}$, outlet pressure of column x ; $u_{i,x}$, inlet velocity of column x ; $p_{o,x}$, outlet velocity of column x .

Using the following limit conditions: $p_{o,1} = p_{i,2} = p_m$ and $u_{o,1} r_1^2 = u_{i,2} r_2^2$, the mid-point pressure p_m between the two GC × GC columns, referred by subscripts 1 and 2, is given by:

$$p_m = \sqrt{\frac{p_{i,1}^2 + m p_{o,2}^2}{1 + m}} \quad (8)$$

where

$$m = \frac{L_1}{L_2} \left(\frac{r_2}{r_1} \right)^4 \quad (9)$$

The split ratio at the tee connection between the GC × GC columns and the retention gap can be defined as:

$$\alpha = \frac{f_{i,1}}{f_{i,3}} \quad (10)$$

where $f_{i,1}$ and $f_{i,3}$ are, respectively, the mass flow at the inlet of the first of GC × GC columns and the mass flow at the inlet of the retention gap. Substituting the velocity by the mass flow ($f = \rho \pi r^2 u$, where ρ is the density), the split ratio can be written as:

$$\alpha = \left(\frac{r_1}{r_3} \right)^4 \frac{L_3}{L_1} \left(\frac{p_{i,1}^2 - p_{o,1}^2}{p_{i,1}} \right) \left(\frac{p_{i,3}}{p_{i,3}^2 - p_{o,3}^2} \right) \quad (11)$$

Taking into account the limit conditions: $p_{i,1} = p_{i,3} = p$ and $p_{o,3} = p_{o,2} = p$ (where p is the pressure at the tee and p_0 the pressure of detectors) and using Eqs. (8) and (9), the relation (11) can be rewritten as:

$$\alpha = \frac{(r_2/r_3)^4 L_3/L_2}{1 + (r_2/r_1)^4 L_1/L_2} \quad (12)$$

As a conclusion, the split ratio only depends on geometrical characteristics of the columns. In particular, it remains constant during the analysis and the temperature changes have no influence on the recovery. The columns geometry used in this study involves that 1.6% of the flow from the olefin trap is directed in the GC × GC columns. Experiments were carried out for decene-1 as a model compound to determine the split ratio as the ratio of areas recorded by FID A and FID B signals. The experimental split ratio was repeatable, equivalent at 30 and 50 °C ($1.35 \pm 0.02\%$ and $1.38 \pm 0.01\%$, respectively), these two temperatures being representative of the temperature range at which the introduction of solutes in the second oven occurs, and similar to the theoretical split ratio.

The recovery was obtained for the olefin trap–GC × GC analysis of the hydrocarbon mixture by normalising the

Table 4

Recovery yields of hydrocarbons from the olefin trap

Number of C atoms	Paraffins	Olefins	Aromatics
8	1	0.84	0.92
9	0.98	0.86	0.95/0.92 ^a
10	0.94	0.86	0.89
11	0.97	0.85	
12	0.93	0.89	
13	0.95	0.86	
14	0.91		

^a Isobutylbenzene/diethylbenzene, respectively.

response of a hydrocarbon against the response of *n*-octane. The response is considered as the ratio of the area corrected by the response factor of the detector to the concentration. As already explained, the area of a peak in GC × GC is considered as the sum of modulated peaks for one compound [17]. For olefins, the area was summed for all isomers. As can be seen from the Table 4, the recovery is high and does not depend on the number of carbon atoms for olefins.

3.7. Application to the GC × GC separation of a heavy naphtha

A heavy naphtha was analysed either by GC × GC after separation in the olefin trap or by GC × GC alone under the conditions given in Table 5. The sample was prepared from the blending of a naphtha cut and of a fluid catalytically cracked (FCC) cut in order to obtain a significant occurrence of all chemical groups. The sample was then diluted in *n*-pentane so that the amount of unsaturate hydrocarbons is compatible with the capacity of the olefin trap (1.4%). Initial contents of olefins and aromatics could have been otherwise determined using methods respectively based on bromine number [18] and UV spectrophotometry [19]. GC × GC chromatograms obtained after separation in the olefin trap and without fractionation are presented in Fig. 6A and B, respectively. The analysis of olefins in such samples is of paramount importance because they are very reactive species in refinery and petrochemistry processes. Despite its high peak capacity, GC × GC fails in separating olefins and saturates as shown in the Fig. 6B because the selectivity of the

Table 5

Operating conditions for the olefin trap–GC × GC separation of a heavy naphtha

	Olefin trap–GC × GC		GC × GC		
Temperature oven #1 trap	180 °C (76 min) + 30 °C/min → 240 °C (20 min)		180 °C		
Temperature oven #2 GC × GC	30 °C + 2 °C/min → 170 °C + 30 °C/min → 30 °C (3.33 min) + 2 °C/min → 170 °C		50 °C + 2 °C/min → 170 °C		
Pressure (kPa)	150		150		
Modulation	0–50 min then 80–130 min (6 s period)		10–50 min (6 s period)		
Time	Valves sequence		Time	Valves sequence	
	V1	V2		V1	V2
0–15	On	Off	0–60	Off	On
15–76	Off	Off			
76–78	Off	On			
80–148	On	On			

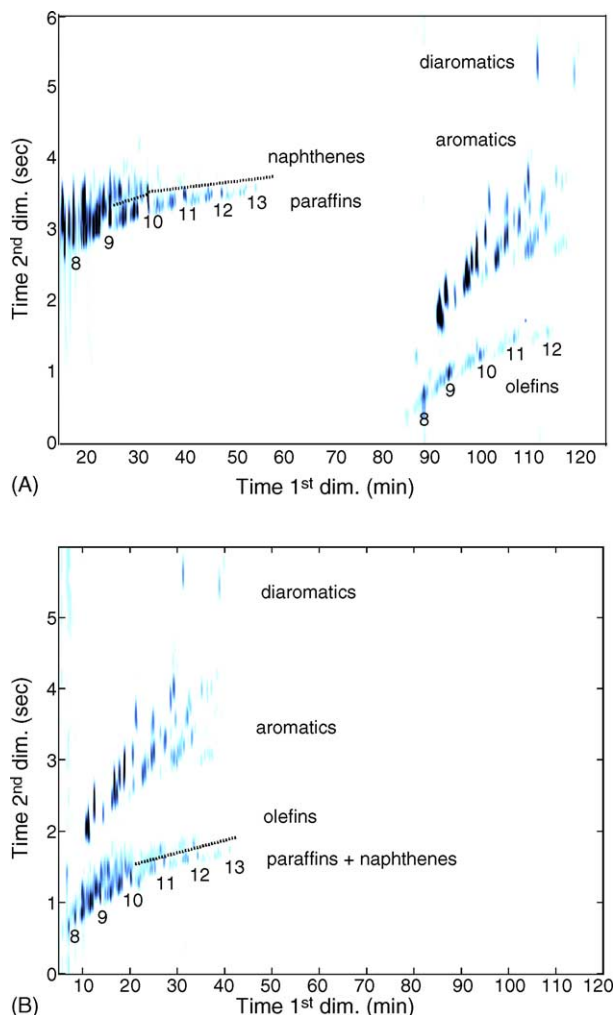


Fig. 6. GC \times GC chromatogram of a heavy gasoline (obtained by blending of a FCC and a naphtha cut) after fractionation using the olefin trap (A) and without fractionation (B). Conditions: see Table 5.

second dimension is not sufficient for the separation of olefins and saturates below C_{10} . Owing to the selective fractionation by the olefin trap, saturate and unsaturate hydrocarbons can be independently analysed by GC \times GC. Thus, it allows the ‘deconvolution’ of the band of olefins from those of saturates, which is an immediate advantage compared to GC \times GC. In the right part of the chromatogram of Fig. 6A, olefins are totally separated from aromatics. Additionally, a detailed separation within a group of olefinic isomers can be obtained. However, the separation between naphthenes and paraffins is still poor for the more volatile compounds ($<C_9$). A higher selectivity between these two chemical classes implies, for example, a longer second column (as shown in [20]) or rather a different stationary phase in the second dimension (e.g. shape selectivity), despite the separation of unsaturates could be badly affected. A trade-off has to be found for the separation of each fraction.

The relative weight content of olefins and aromatics was obtained using the response factors determined for standard compounds. The repartition according to the number of car-

Table 6

Relative weight content of olefins and aromatics in the heavy naphtha

Number of carbon atoms	Olefins	Aromatics
8	1.92 ± 0.07	11.4 ± 0.36
9	2.04 ± 0.06	9.32 ± 0.31
10	1.42 ± 0.04	6.25 ± 0.17
11	0.94 ± 0.03	3.02 ± 0.09
12	0.65 ± 0.03	0.79 ± 0.03
13	0.22 ± 0.01	0.02 ± 0.01

The olefin trap-GC \times GC separation conditions are reported in Table 5.

bon atoms is given in Table 6. A better level of confidence can be given to the olefin trap-GC \times GC detailed separation, because the risk of assigning a compound to the wrong chemical group is reduced. The detailed characterisation of hydrocarbons according to the chemical group and to the number of carbon atoms becomes now possible in the C_8 – C_{14} range, but the individual identification is still limited, especially for olefins owing to the high number of possible isomers in this volatility range.

4. Conclusion

The hyphenation of an olefin trap to GC \times GC is a novel way to perform the detailed analysis of hydrocarbons in the C_8 – C_{14} range. This approach demonstrates an excellent resolution between all chemical groups in complex naphtha and it can be regarded as an innovative solution to answer the delicate problem of the determination of olefins in such samples. Extended capabilities of the olefin trap were demonstrated with the analysis of unsaturates, olefins and aromatics, through C_{14} . The on-line transfer of analytes between the trap and the GC \times GC analytical columns is an advantage to avoid sample losses compared to off-line procedures. This study also pointed out the limitations of the method. The main limitation is related to the capacity of the trap, which prevents the analysis of naphtha with a high content of unsaturate compounds, unless dilution does not affect the detection of minor components. Besides, this method is limited to relatively narrow cuts, not exceeding 8 carbon atoms, boiling up to 250°C , which prevents the analysis of diesel samples. At last, the conversion/isomerisation of olefins at the temperature of their trapping/desorption is another drawback.

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