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# Comprehensive two-dimensional gas chromatography for enhanced analysis of naphthas: New column combination involving permethylated cyclodextrin in the second dimension

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**Abstract**

A new column association using comprehensive two-dimensional gas chromatography for the detailed molecular analysis of hydrocarbon mixtures is reported in this paper. In order to compare the impact of two different secondary columns, a novel column combination relying on a GC × 2GC system was used. This system is based on a non-polar first column (PONA) combined with both a permethylated β-cyclodextrin (β-Dex 120) stationary phase and a polysilphenylensiloxane (BPX 50) in the second dimension. Compared to BPX 50 stationary phase, the implementation of β-cyclodextrin columns as the second dimension was found to improve the resolution between paraffins and naphthenes in the naphtha range but not in the middle distillate range. Attempts to improve the results and to understand the interaction mechanism remained unsuccessful. Therefore, the benefits of the β-Dex 120-column are only demonstrated on heavy naphtha cut for the quantitation of hydrocarbons.

*Keywords:* Gas chromatography; Comprehensive two-dimensional GC; Multidimensional GC; β-Cyclodextrin; PIONA analysis; Unsaturated hydrocarbons; Heavy naphtha; Hydrocarbons

## 1. Introduction

Owing to the growing demand for fossil fuels, there is a strong need for more detailed analysis of their composition in order to (i) understand better the transformation processes occurring during the valorization process, (ii) improve kinetics and thermodynamics models used to optimize refining processes and (iii) to control the specifications of the products.

Attempts to obtain detailed hydrocarbon analysis (DHA) of petroleum cuts and refining products started in 1970s using either mass spectrometry or high-resolution gas chromatography (HR-GC). As mass spectrometry does not allow for sufficient molecular recognition [1], gas chromatography has been intensively used to reach the DHA. It has been coupled with universal detectors such as flame ionization detector (FID) as well as with specific or informative detectors such as chemiluminescence or mass spectrometry (MS) in order to further improves the selectivity.

Even though the hyphenation of informative detectors drastically simplified the interpretation of chromatograms, HR-GC still suffers from a lack of resolution between paraffins, olefins and naphthenes (i.e. cyclic-alkanes) which cannot be solved by the hyphenation of MS [2,3]. HR-GC also lacks peak capacity for mixtures containing compounds above C9 for straight run distillates and even less for mixtures containing high levels of olefins [4].

In order to improve the peak capacity, multidimensional gas chromatographic systems were investigated. The so-called PNA [5] and PIONA (paraffins, isoparaffins, olefins, naphthenes, aromatics) analyzers were developed. They provide a fractionation according to chemical classes and within a class, a separation of compounds according to the carbon number up to C11 in

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one injection. Nevertheless, owing to the implementation of molecular sieves, this strategy is limited to gasoline and cannot be extended to heavier cuts [6].

Comprehensive gas chromatography (GC × GC) provides unequalled separations of petroleum samples [7] owing to its increased peak capacity [8], resolution power and increased sensitivity [9]. However, comprehensive two-dimensional gas chromatography still lacks selectivity to fully resolve olefinic hydrocarbons from naphthenes and paraffins. Recently, silver(I) impregnated silica was used by Vendeuvre et al. [7] to selectively trap unsaturated hydrocarbons prior to GC × GC analysis. This trap allowed unsaturated and saturated hydrocarbons with a carbon number below 15 to be analyzed separately using GC × GC. However, separation between naphthenes and paraffins was not improved and no accurate quantification of naphthenes in heavy naphtha (C8–C15) and middle distillates (C13–C23) could be achieved.

In order to improve the selectivity between naphthenes and paraffins in the C8–C23 range, a new GC × GC approach is investigated. It is based on the implementation of permethylated cyclodextrins as the second dimension stationary phase. β-cyclodextrins are cyclic, torus-shaped macromolecules composed of D(+)-glucose residues bonded through α(1,4) glucosidic linkage [10]; they are known for size and shape discrimination involving host (the cyclodextrin) and guest mechanism [11].

The first part of this paper deals with the evaluation of the limitations of this approach using the resolution between naphthenes and paraffins in the full range of carbon atoms (C8–C23). In the second part, the benefits of implementing a cyclodextrin column are demonstrated for the analysis of heavy naphthas using a fluid catalytic cracked (FCC) cut.

## 2. Experimental

### 2.1. GC × 2GC setup

In order to evaluate the impact of the nature of two different secondary stationary phases on the paraffins/naphthenes separation a GC × 2GC system was used. In this respect, same conditions of separation (same flow rate, same column feature, and same temperature) except the nature of the stationary phase could be achieved in each second dimension studied. The GC × 2GC system is a modified standard gas chromatograph HP6890N (Agilent Technologies, Massy, France). In this work, the GC × 2GC analysis was carried out with two secondary columns as already described by Seeley et al. [12]. Using a universal Y splitter (Restek, France), a non-polar column (PONA, Agilent Technologies, Massy, France, 15 m, 0.2 mm, 0.5 μm) in the first dimension was connected to two parallel secondary columns: BPX 50 ((50% phenyl)-polysilphenylen-siloxane, SGE, France) and β-Dex 120 (20% permethylated β-cyclodextrin in a SPB 35 matrix, Supelco, France). The dimensions of both secondary columns were identical (1.0 m, 0.1 mm ID, 0.1 μm). Owing to phase distribution (film thickness) differences in the second dimension, repeatability problems may arise. Therefore, all experiments have systematically been repeated three times using different pieces of secondary columns to ascertain results.

Table 1A
Operating conditions of the GC × 2GC system

| GC × 2GC operating conditions | |
|---|---|
| Temperature oven | 50 °C + 3 °C/min → 240 °C (20 min) |
| Pressure | 250 kPa |
| Modulation period | 12 s |
| 1st dimension column | PONA (15 m, 0.2 mm, 0.5 μm) |
| 2nd dimension columns | BPX 50 (1.0 m, 0.1 mm, 0.1 μm) AND β-Dex 120 (1.0 m, 0.1 mm, 0.1 μm) |

It was shown in [7] that the flow rate in two parallel columns only depends on the dimensions of the columns. For an overpressure of 250 kPa applied at the inlet of the first column, the flow measured at the outlet of each second dimension column was 1 mL/min at room temperature. Using the model proposed by Vendeuvre et al. [13], it was shown that, under operating conditions previously described, carrier gas velocity was 46.6 cm/s and 143 cm/s in the first and both second columns, respectively. Of course, from the chromatographic point of view, the secondary separation is achieved far above optimal conditions. However, one should keep in mind that a compromise has to be reached to (i) achieve a fast enough secondary separation in order to prevent wrapping around and to (ii) separate compounds of interest according to the second dimension. This also means that the secondary column can hardly be operated close to optimal chromatographic conditions.

The two secondary columns were fixed using two-hole ferrules (Varian, France) on the modulator support. The modulator was a dual stage carbon dioxide jet modulator built in house as described by Beens et al. [14]. In order to avoid vibrations of the columns, a septum was placed between the two carbon dioxide jets to hold the two columns together.

Two FID detectors set at 320 °C were used for detection. $H_2$, air and He (make up) flows were respectively 35 mL/min, 400 mL/min and 25 mL/min. The scheme of the whole apparatus is depicted in Fig. 1A and the operating conditions are reported in Table 1A.

### 2.2. Hyphenation of the unsaturated hydrocarbon trap

In order to analyze sequentially the saturated and unsaturated fractions of the samples, a silver impregnated silica trap (Analytical Controls, Rotterdam, The Netherlands) was hyphenated to the GC × GC system (Fig. 1B). The trap was installed in the oven of a model 5890 gas chromatograph (Agilent Technologies, Massy, France) so that its temperature could be controlled. Helium was provided to the injector of the first chromatograph by the auxiliary channel (Electronic Pressure Control) of the second chromatograph to ensure a constant pressure during the analysis (150 kPa). Two 6-way valves (Valco) were installed in a heated block in the first chromatograph to enable the backflush, foreflush and the isolation of the trap to take place. The different modes were obtained by activating specific valves whose configuration is presented in Fig. 1B. An insulated transfer line went