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Comparison of conventional gas chromatography (1D-GC) and comprehensive two-dimensional gas chromatography (GC×GC) for the detailed analysis of petrochemical samples

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Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) has been investigated for the characterization of high valuable petrochemical samples from dehydrogenation of n-paraffins, Fischer Tropsch and oligomerization processes. GC×GC separations, performed using a dual-jets CO₂ modulator, were optimized using a test mixture representative of the hydrocarbons found in petrochemicals. For complex samples, a comparison of GC×GC qualitative and quantitative results with 1D-GC has demonstrated an improved resolution power of major importance for the processes : the group type separation has permitted the detection of aromatic compounds in the products from dehydrogenation of n-paraffins and from oligomerization, and the separation of alcohols from other hydrocarbons in Fischer Tropsch products.

Key words: gas chromatography, comprehensive two-dimensional, petrochemistry, petrochemical

1-Introduction

Since its introduction in the 1990's, comprehensive two-dimensional gas chromatography (GC × GC) has demonstrated very promising perspectives for the analysis of complex mixtures. The main reason lies in the higher peak capacity obtained with the combination of two chromatographic columns that develop complementary selectivities so that the entire sample is submitted to two orthogonal separations. The description of the separation mechanisms as well as the principle of modulation have been widely reported in previous papers [1,2]. Technical innovations concerning modulators (mainly heating and cryogenic systems) have been decisive for the use of GC×GC by an increasing number of analysts : its relative simple implementation enables its hyphenation in systems involving a sample pretreatment step, specific detection or mass spectrometry (MS) detection. For instance, atomic emission detection (AED) [3] and sulfur chemiluminescence detection (SCD) [4] have been recently associated to GC×GC.

Petroleum was one of the first fields of application investigated in GC×GC. The high peak capacity was expected to enhance the limited resolution obtained with a single chromatographic GC column (1D-GC) when analysing samples containing hydrocarbons having more than 9 carbon atoms. As petroleum samples may contain several thousands of components, the individual identification of the entire sample is a unrealistic task whatever the analysis technique employed and may be useless considering the effective level of characterization that is needed. Actually, emphasis is generally put on PIONA group type separation (standing for Paraffins, Isoparaffins, Olefins, Naphtenes and Aromatics) and carbon number. One of the goals is to deduce from a structural information macroscopic properties such as octane numbers that measure the combustion performances of fuels. Up until now, GC×GC has been used in order to provide a more detailed composition of petroleum samples originating from refining (mostly kerosene [5,6,7]) as well as from geochemistry (oil spill

identification [8], biomarkers in petroleum[9]). Two-dimensional chromatograms highlighted the complexity of these samples through the impressive number of peaks. However, owing to the two different separation mechanisms involved with two different columns according to polarity and volatility, the organization of chromatograms versus the structure of compounds (the well-known roof tile effect [5]) enables bands of isomers to be easily recognized. In this way, the individual identification can be avoided if the only needed information is the PIONA distribution versus the carbon number.

When looking at the literature [10], the majority of applications of GC×GC in the oil industry refers to petroleum or fractions obtained from refining. Today, petrochemistry plays a major role as a link between the petroleum industry and the speciality industries (drugs, paints, cosmetics) that produce high valuable products. However, only a few applications of GC×GC to petrochemicals have been proposed so far. Compared to petroleum samples, these products are less complex because they are synthesized from relatively well characterized reactants obtained from petroleum or natural gases. Though, the resolution of separations obtained in 1D-GC is limited, partly because olefins, encountered in these samples since they are often used in petrochemistry on account of their reactivity, are poorly or not resolved from other hydrocarbons.

The aim of this work is to evaluate the potential of GC×GC for the detailed analysis of petrochemical samples. A comparison with 1D-GC will be presented, both techniques being performed under their own optimal conditions.

2. Experimental

2.1. Equipment

2.1.1. GC×GC

i) Hardware

GC×GC was performed using a HP6890N chromatograph and its acquisition software *ChemStation* (Agilent Technologies, Massy, France). A dual-stage carbon dioxide jet modulator, built in-house as described by Beens *et al.* [11], was adapted in the chromatograph. It comprises two valves (Asco Joucomatic, Rueil Malmaison, France) electrically driven by an interface synchronized with the chromatograph. GC×GC analyses were carried out using a 4 seconds modulation period.

ii) Columns

In the first dimension, a dimethylpolysiloxane column was used (PONA, Agilent) (Table 1). For optimization purpose, different columns were used in the second dimension, either a (50%phenyl)-polysilphenylene-siloxane (BPX50, SGE, Courtaboeuf, France), a (70%cyanopropyl)-polysilphenylene-siloxane, (BPX70, SGE) or a polyethyleneglycol (CPWax, Varian, Les Ulis, France). As the modulation takes place upstream from the second column, the launch of trapped materials occurs 10 cm after the connection between the two columns. Therefore, the useful length of the second column for separation has to be reduced by 10 cm. However, for flow calculations, the total length of the second column was used. Both columns, connected through a 0.2 mm glass press fit (Agilent Technologies), were placed in the same oven that was temperature programmed at 2 or 5°C/min from 50°C to 250°C.

iii) Pressure

Helium (99.99%, Air Liquide, Feyzin, France) was used as the carrier gas at constant pressure through both columns during the analysis run.

Other experimental conditions are summed up in Table 1.

iv) Data processing

Raw data were processed by a dedicated program written in-house under MatLab 6.5. Input data – csv type file (10-50 Mbytes) exported from ChemStation and the modulation period – are transformed into two-dimensional color plots. Intensity of peaks is displayed with a colour gradation and the contrast can be modified by setting threshold values of intensity.

2.1.2. 1D-GC

A synthetic PIONA mix and three petrochemical samples were analysed in 1D-GC using conditions detailed in Table 2. Results were further processed with a dedicated software (Carburane®) based on automatic peak identification using a retention indice database.

2.2. Chemicals

The PIONA test mixture, prepared using standards purchased at Fluka (Seelze, Germany), contained 17 hydrocarbons : normal and iso-paraffins, olefins, naphtenes, aromatics and naphtheno-aromatics, with boiling points ranging from 164 to 198°C. They were each diluted in n-heptane at about 100 µg/L. Petrochemical samples were provided by IFP pilot units developing the following processes : dehydrogenation of normal paraffins, Fischer Tropsch and oligomerization.

3. Results and discussion

3.1. PIONA test mixture

Using a synthetic PIONA mix, the efficiency of cryofocussing and the resolving power of our GC×GC prototype were evaluated for comparison with the results published in the literature and with 1D-GC according to resolution, detection limits and quantification.

3.1.1. Influence of chromatographic conditions on resolution

A 4 seconds modulation period was chosen because a minimum of 3-4 samples across primary peaks of 15 seconds width are required, as stated elsewhere [12]. Although the separation of the first column in GC×GC is less efficient than in 1D-GC owing to its reduced length, GC×GC provided better overall resolution of the synthetic PIONA mix. Three column combinations (BPX50, BPX70, CPWax) were compared. CPWax provided the best overall separation, which was confirmed by the value of resolution (R_s) calculated using Giddings formula [13] : for all compounds resolution was above 1.2. However wrapping around of naphtheno-aromatic compounds (indene) occurred when CPWax was used. Optimization of operating conditions for samples containing various hydrocarbon chemical families (with paraffins and naphtheno-aromatics) showed that the combination of slower temperature programming (at 2°C/min) and BPX50 in the second dimension provided better separation with chromatograms well structured. Moreover, BPX50 is the only available stationary phase compatible with the analysis of hydrocarbons of more than 25 carbon atoms owing to its high maximum operating temperature of 360°C.

3.1.2. Signal/Noise

Signal/Noise (S/N) values obtained in GC×GC for the PIONA mix were 4 to 10 times greater than those calculated in 1D-GC, despite the higher acquisition frequency (100 Hz instead of 5 Hz); this is a real advantage for the detection of traces in complex matrices. Detection limits, determined at S/N=3, were between 10-21 pg in GC×GC and 76-97 pg in 1D-GC. As a comparison, Dallüge *et al.* [14] reported detection limits of 5-23 pg with GC×GC-TOFMS, and S/N improvement by a factor 4-7. Note that the determination of S/N values should be carefully examined in GC×GC because S/N does not only depend on concentration like in 1D-GC, but also on the modulation period and on the phase shift as pointed out by Ong *et al.* [15].

3.1.3. Quantification

Quantification of the synthetic PIONA test mixture was undertaken as an additional element of comparison between GC×GC and 1D-GC. As it has been already reported [16], integration in GC×GC is achieved using the raw chromatogram by summing the areas of each modulated peak originating from the same compound. Combination of modulated peaks has been manually performed. Relative standard deviation calculated for GC×GC analyses of the PIONA test mixture in three replicates was in the range 0.1 to 1.8%. The relative difference between GC×GC and 1D-GC results was lower than 3%. Two compounds coeluted in 1D-GC could be easily quantified in GC×GC because they were baseline separated in the second dimension. These measurements are in full agreement with previous findings [16] and one can conclude that GC×GC enables as good quantitative analysis as 1D-GC, at least for a simple mix.

3.2. Application to complex petrochemical samples

3.2.1. Dehydrogenation of normal paraffins

Linear olefins are widely used in petrochemistry owing to their high reactivity. For example, they are used as alkylation reactants for the production of alkylbenzenes (surfactants). They are usually obtained by dehydrogenation of normal paraffins with a low conversion yield (maximum 20%). By-products such as aromatics and diolefins are also produced ; the content of diolefins and aromatics should be limited because the formers can form gums in the samples and the latters are catalyst inhibitors. Qualitative and quantitative informations on the composition of these products are needed to optimize the process through a better understanding of thermodynamics. Presently, 1D-GC enables neither the detailed analysis nor the determination of the chemical classes of these fractions mainly because some fractions coelute : aromatics and diolefins, isoparaffins and olefins.

Even GC-MS cannot solve this problem as deconvolution of mass spectra at trace level is not possible.

Figure 1 shows GC×GC chromatograms of the feed (A), and the products of conversion of n-paraffins into n-olefins at 10% (B) and at 20% (C) yields. Experimental conditions are given in Table 1. The feed mainly contains n-paraffins from decane to tetradecane. With a glance at Figure 1-B and 1-C, the formation of two novel chemical classes of greater polarity than n-paraffins is obvious after conversion. According to the preliminary study with the PIONA mix using the same experimental conditions, these compounds were assigned to aromatics and diaromatics. A deeper insight in the structure of the chromatogram shows a repetitive pattern of compounds, enhanced in the insert of Figure 1-C. Isoparaffins elute slightly earlier than n-paraffin in each dimension. The rules of retention described elsewhere are observed [5] : isoparaffins more volatile than n-paraffins due to lower Van der Waals interactions elute in the first dimension before n-paraffins. Because of their reduced molecular area, the interaction of isoparaffins with the semi-polar second dimension stationary phase is slightly lower than that of n-paraffins. Olefins are separated from n-paraffins only in the first dimension, the selectivity of the second dimension being too low to improve this separation. On the contrary, diolefins are more retained in the second dimension than n-paraffins. Most polar hydrocarbons, aromatics and diaromatics, have the highest retention times and are located in the upper part of the chromatogram.

Unsaturated compounds are not detected in the feed: they are formed during the process. This information is of major importance for the process and has to be implemented in thermodynamics studies to understand the conversion of a completely saturated chain into a diaromatic molecule that contains as many as seven insaturations. Figure 2 compares parts of chromatograms obtained in 1D-GC and in GC×GC where the elution zone between n-undecane and n-dodecane has been

highlighted. Enhancement of S/N and higher resolution owing to the second semi-polar column allowed naphthalene to be easily identified in GC×GC.

Quantification was compared between 1D-GC and GC×GC for the determination of n-paraffins. Even if split injections are achieved, discrimination was not likely to occur owing to the limited boiling point range of the samples. Results were expressed as a relative weight content in the feed and the products of conversion. An excellent agreement between both techniques was found for n-paraffins : 98.4% determined in the feed by both techniques. The relative weight content determined by GC×GC and 1D-GC was respectively 89.1% and 90.1% in the product converted at 10%, and 80.3% and 80.6% determined in the product converted at 20%. Owing to its higher resolution power compared to 1D-GC, GC×GC allowed the determination of the repartition in weight content of the different chemical families, for example, for hydrocarbons with 12 carbons, whose elution zone is reported in Figure 1. In the product converted at 10%, n-paraffin represents 90.1%, olefins 8.4%, isoparaffins 0.7%, diolefins 0.4% and aromatics 0.3%; in the product converted at 20%, n-paraffin represent 80.6%, olefins 14.5%, isoparaffins 0.6%, diolefins 1.2% and aromatics 4.5%. These results highlight the disappearance of n-paraffins while olefins, aromatics and diolefins are formed during the process. The repartition of the different chemical species easily obtained by GC×GC and the accurate determination of the relative weight contents constitute a decisive advantage for the process.

3.2.2. Fischer-Tropsch process

Fischer-Tropsch synthesis, developed in the 1920's, has recently met a renewed interest since petroleum reserves are known to be limited to some decades. In the present context of higher energy demand with more environmental concern, alternatives to petroleum are being developed. Fischer Tropsch technology converts coal, natural gas and low value refinery products into high value clean

products. Normal paraffins are the main products formed from hydrogen and carbon monoxide. They can be used for wax production but can be more readily upgraded to fuels. Subsequent hydrocracking / hydroisomerisation of Fischer Tropsch products improve their thermal properties at low temperature to allow their blending in a diesel pool. Actually these resulting « green » fuels containing no sulfur and no aromatics present good combustion characteristics (with a high cetane number). During Fischer Tropsch process, other products are formed: isoparaffins, olefins and alcohols. A detailed analysis of a Fischer Tropsch sample has been achieved in GC×GC and in 1D-GC using experimental conditions given in Table 1 and Table 2. In 1D-GC, alcohols were coeluted with isoparaffins. This obviously leads to a conflicting integration. Moreover, only primary linear alcohols were identified in 1D-GC.

Figure 3 presents the GC×GC chromatogram of a Fischer Tropsch product. At a first sight, two bands are identified : paraffins, olefins and isoparaffins are located in the first lower band whereas alcohols, more retained on BPX50, form the upper band. Besides, GC×GC provides an enhanced information on sample composition because it allows the detection of about four isomers of alcohols at a given carbon number, eluting at the same second dimension retention time. The position of the hydroxy function is not precisely identified and this should be evaluated in the next future using hyphenation with Time Of Flight Mass Spectrometry. Quantitative results were compared between 1D-GC and GC×GC for n-paraffins, from n-nonane to n-pentacosane. Relative deviations between normalised peak areas of n-paraffins determined in 1D-GC and GC×GC were in the range 0.1-3.3%. GC×GC enables the determination of the contents of each chemical family per carbon number while 1D-GC cannot owing to coelution. For instance, the relative weight content determined for compounds located in the insert of Figure 3 (hydrocarbons with 11 carbon atoms, alcohols with 8 carbons) is as follows: 73.1% n-paraffin, 19.2% olefins, 2.1% isoparaffins and 5.6% alcohols (4.7% are primary alcohols).

3.2.3. Oligomerization

Oligomerization of monomers is an interesting way to produce branched olefins mainly used for gasoline, kerosene and diesel oil. This process consists in the repeated addition of the butene molecule to itself to form a heavier olefin mixture from 8 to 20 carbon atoms. A sample of oligomerization was analysed in 1D-GC using experimental conditions in Table 2: olefins and isoparaffins were found to represent respectively 92.5% and 7.5% of the sample. However, some suspicions remained concerning the presence of aromatics. In order to check this assumption, the sample was analysed by GC×GC. Experimental conditions are reported in Table 1 and the chromatogram is presented in Figure 4. The wide band is attributed to olefins, with a distribution centered on olefins with 12, 16 and 20 carbon atoms. Quite surprisingly, isolated peaks, at trace level, having a higher second dimension retention time than those of olefins could be clearly visualized: they are bordered with a dotted line in the chromatogram. They were attributed to alkylbenzenes using PIONA test mixture results obtained with the CPWax column in the second dimension. Alkylbenzenes formation probably comes from hydrogen transfer between olefins to form isoparaffins with a lower carbon number and aromatics with a higher carbon number. Isoparaffins could not be quantified owing to the lack of selectivity of the second dimension; the weight content of each alkylbenzene was in the range 0.002-0.01 % leading to a total weight content of 0.27%. This determination is of major importance for the process as aromatics at these low concentrations were undetected in 1D-GC because they coelute with olefins present at a much higher content. Again, GC×GC shows a decisive advantage for the determination of minor classes of hydrocarbons at trace level. It is an alternative method to UV spectrometry or Near InfraRed for trace analysis of aromatics in middle distillates.

4. Conclusion

The enhancement of resolution associated with the high peak capacity, the structure of the chromatograms and the higher sensitivity are the main advantages of GC×GC for a more detailed analysis of complex petrochemicals leading to a better understanding of the processes. The separation of aromatics in the products of deshydrogenation of n-paraffins and of alcohols in Fischer Tropsch products from the paraffinic matrix allowed the precise determination of their content. Determination of aromatics at trace level in the olefinic matrix of oligomerisation process is not possible by any other separation method.

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