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Comprehensive Two-Dimensional Gas Chromatography and Its Application to the Investigation of Pyrolytic Liquids

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Additional information is available at the end of the chapter

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Abstract

The chapter presents basic principles of one-dimensional gas chromatography (1D-GC) and comprehensive two-dimensional gas chromatography (GC \times GC) related to the main advantages of the two-dimensional technique, as well as its application to the study of organic compounds in liquids derived from coal, mainly through pyrolysis and extraction. It also shows the investigation of compounds contained in bio-oils obtained from biomass through pyrolysis, using GC \times GC. Advances in scientific knowledge related to the composition of these complex matrices are shown through different examples of GC \times GC analyses, such as the identification of trace compounds that would not be perceived by 1D-GC, organized patterns of elution of structurally related compounds that help their identification, etc. Examples shown make it clear that GC \times GC is the technique of choice to elucidate composition of these complex matrices.

Keywords: comprehensive two-dimensional gas chromatography, GC \times GC, pyrolysis, bio-oil, coal tar, coal bitumen, mass spectrometry

1. Introduction

Gas chromatography (GC) or one-dimensional gas chromatography (1D-GC) is a mature technique that offers high peak capacity and complementary data provided by different detectors. It has been successfully applied to several areas of knowledge, which confirms its maturity as an

analytical technique. However, several matrices are so complex that 1D-GC may not be capable of separating their components, such as petroleum and derivatives, natural aromas, perfumes, foods and beverages, environmental samples, etc. One aspect that makes it even more difficult is the presence of compounds in trace concentrations that co-elute with other components of interest or with matrix interferences that are present in larger amounts in a sample. Such a situation is commonly seen in complex matrices as the ones formerly mentioned. It is especially cumbersome when the trace compound plays an important role in the sample under investigation, and some examples may be mentioned on this regard: nitrogen and sulfur compounds in petroleum, coal tar and bitumen, aroma active compounds in wine aroma, allergens in perfumes, etc. Misidentification, wrong quantification of important compounds may arise from such a situation and consequently false results that might lead to wrong decisions. In addition, high-quality mass spectra with no interferences are a difficult goal to achieve in 1D-GC, although specific detectors may be of help when some chemical groups are being target.

Several trials have been made to improve chromatographic resolution (R_s) in 1D-GC, according to the following equation:

$$R_s = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k}{1 + k} \right) \quad (1)$$

where N is the number of plates, α is the separation factor of a pair of solutes, and k is the retention factor of the most retained solute [1].

One alternative is to extend the length of the chromatographic column, however, as R_s is a function of the quadratic root of N ; this strategy ends up in time-consuming analyses, larger peak base width and consequently higher detection limits. A classical illustration is the analysis of gasoline made by Berger in a 550 m long chromatographic column (1.3 million effective plates) where 970 compounds were separated, although not all compounds of this sample were resolved. Analysis time was eleven hours, and this example makes it clear why such a time-consuming approach is not welcome [2].

Alternatively, it is possible to employ smaller column diameters, which are associated with high carrier gas flow and higher oven heating rates in fast GC. However, resolution observed in fast GC chromatograms is usually similar to conventional ones, except that analysis time is shorter [3, 4]. In summary, with the before mentioned equation of chromatographic resolution in mind, it seems that the most effective way of improving resolution is to modify the separation factor (α), and this can be accomplished using multidimensional gas chromatography, with different stationary phases. Two conditions define multidimensional separation techniques: (1) the components of the sample subjected to two different mechanisms, and (2) components should remain separated until the end of the separation process [5–7]. Two-dimensional gas chromatography (2D-GC) may be classified as heart cutting (GC-GC) and as comprehensive (GC \times GC). In GC-GC, only some parts of the effluent from the first chromatographic dimension (1D) are introduced in the second dimension (2D). It is of special interest when only target components are the focus of the study, but not when the whole sample is under investigation. The length of the second column is conventional, and runs in this dimension are independent of the analysis in 1D . The longer the number of chromatographic band cuts, the longer the analysis time, as every cut has to undergo a further separation in the second dimension, adding extra time to the complete analytical process. In particular, care

should be taken, as cuts should not be too long, otherwise compounds that have already been separated in 1D may be mixed again before reaching the 2D column [8]. In GC \times GC, all the effluent from 1D or a representative part of it is lead to 2D , while the separation achieved in the first dimension should be maintained. The analysis time is the same as the one of 1D run, and second dimension runs occur at same time in which 1D analysis is running [9]. The goal of this chapter is to present some fundamental aspects of GC \times GC and the advantages of its application to the investigation of pyrolytic liquids from coal and biomass, as well as of bitumen.

2. Comprehensive two-dimensional gas chromatography (GC \times GC)

Comprehensive two-dimensional gas chromatography (GC \times GC) started in 1991, due to the brilliant contribution of Professor John Philips and his research group [10]. Even though it is a relatively young technique, it has already experienced several stages of development and is maturing in a fast pace. The first applications of GC \times GC were related to petrochemical samples [11, 12]; however, other applications have followed these preliminary ones, such as forensic samples [13], environmental samples [14] food samples [15, 16], petroleum and derivatives [17] etc. The fractions coming from 1D [typically 15–60 m of length, 0.25–0.32 mm of internal diameter (1dc) and 0.1–1 μm of film thickness (1df)] are sampled and focused in the modulator and further transferred to 2D . The second column is shorter [commonly 0.5–2 m of length, 0.1–0.18 mm of internal diameter (2dc) and 0.1 μm of film thickness (2df)] to allow fast separation of the sequential chromatographic bands.

Figure 1(A) schematically illustrates a general GC \times GC equipment. The stationary phases of both columns should be of different natures and should be chosen according to the dimensionality of the sample [18]. If the column in the 1D is of nonpolar nature, the stationary phase of the second column should take profit of another mechanism of separation, such as, polar interactions (e.g., π - π interactions, among others). This type of column set is designated “conventional” and was the most common in the early applications of GC \times GC. When the 1D is polar and the 2D contains a nonpolar stationary phase, the column set is called “inverse” set. Modulation is the key process of GC \times GC, and the modulator is located in between the two columns, at the end of the 1D or in the beginning of the 2D . **Figure 1(B)** illustrates the modulation process with a cryogenic liquid. The modulator provides sampling and concentration of the chromatographic bands eluting from 1D and leads these bands to a fast separation in 2D [18].

The modulator collects the chromatographic band eluting from the 1D during a preset period of time (**Figure 1(B)** B1). The modulator chosen for illustrative purposes in the example presented in **Figure 1(B)** is a double jet cryogenic modulator. When the modulator is actuated (**Figure 1(B)** B1), a cooled nitrogen gas jet is directed to a small area of the modulator. During this period of time, the chromatographic band undergoes compression and is narrowed due to the low temperature of the refrigerating fluid, and the narrower band is introduced in the 2D as a short pulse (**Figure 1(B)** B2). Therefore, the analytes are concentrated enhancing the chromatographic analysis sensitivity and resolution. The chromatographic band release is provided by a hot jet in the same region of the capillary or only due to the heating provided by the chromatographic oven. At the end of a modulation process, a new fraction of 1D effluent

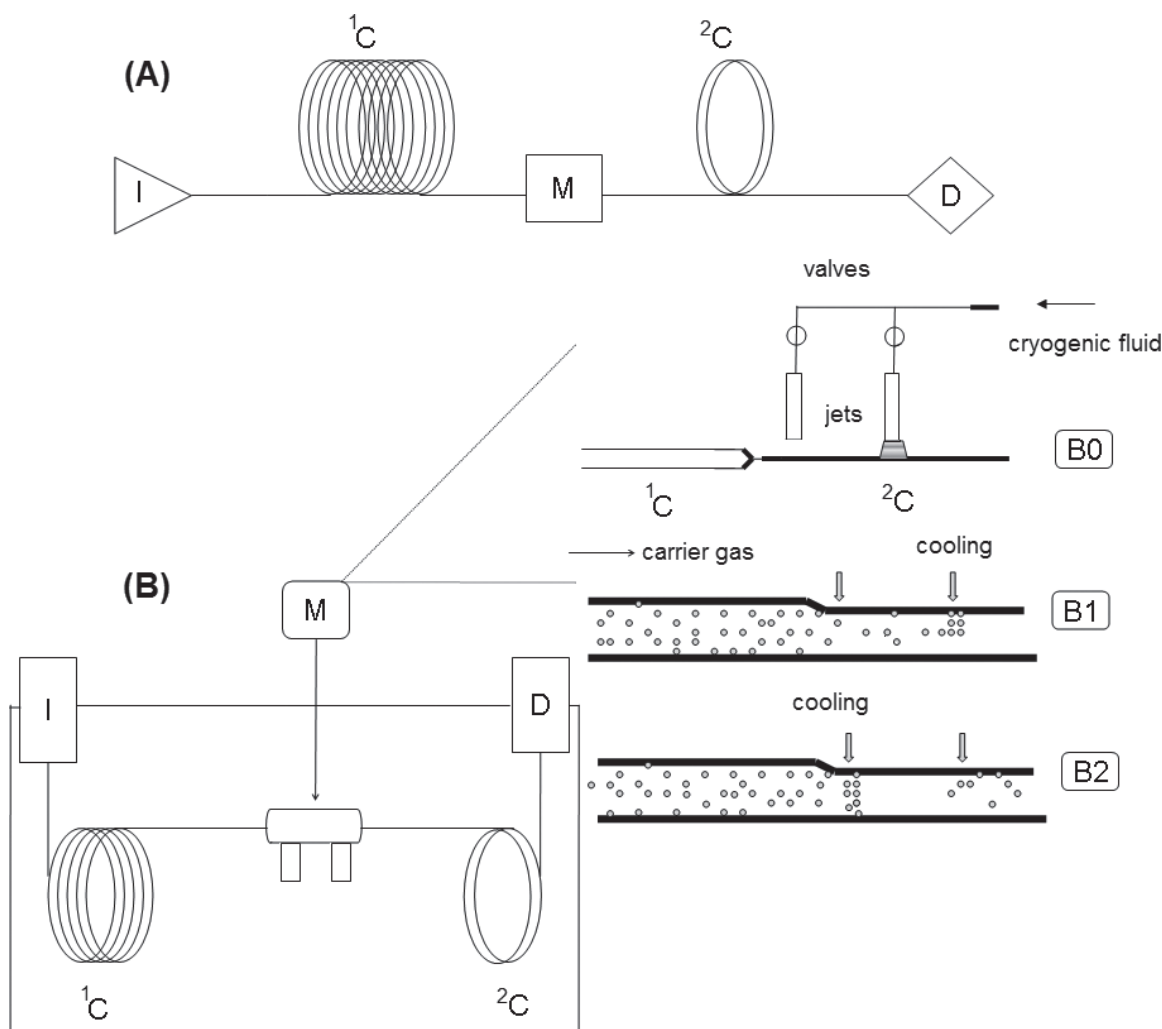


Figure 1. Representative schemes of a GC \times GC system. (A) Main parts of a GC \times GC equipment. (B) Illustration of a double jet cryogenic modulation system (adapted from Dalluge et al. [19]).

enters the modulator (the flow from 1D is continuous), while the former fraction undergoes a fast separation in the 2D column. This process of sampling, focusing, and release of the continuous chromatographic bands eluting from 1D occurs during the whole GC \times GC analysis. A complete cycle of modulation is called period of modulation (P_M), and this time period is equal to the 2D run time. At the end, the compounds that elute from 2D pass through the detector and a series of short 2D chromatograms are obtained. The technique is called “comprehensive” because all the effluent coming from 1D is transferred to the second dimension.

Modulators are classified according to its operating principle in thermal and flow modulators. Thermal modulators are the ones where a positive and/or negative difference in temperature is employed to achieve modulation [20–22]. The example given refers to a thermal modulator that employs a cryogenic system. It provides high efficiency of band focusing and further fast release of chromatographic bands [23]. There are several different designs of cryogenic modulators that employ refrigerating liquids (nitrogen or carbon dioxide), such as the one with a cold double jet (example given above) [8], the one with four jets (two cold and two hot jets) [24] the loop modulator [25] etc. Carbon dioxide is an efficient cooling liquid; however, if

compounds under study are too volatile (less than six carbons), liquid nitrogen is considered to be more appropriate [23]. Even though cryogenic modulators are well known for its high efficiency, flow modulators are simple and low cost devices, as they do not require the use of a cryogenic fluid. Flow modulators have been the focus of intense research in the last few years and are becoming an alternative, especially for routine analyses. A more complete discussion on this subject is available in review and research articles elsewhere [21, 22, 24].

In order to preserve the separation obtained in the first dimension, sampling fractions should not be longer than $\frac{1}{4}$ of the widths of the peak in 1D [26, 27] in 2D are in the range of 2–8 s and so, runs are essentially isothermal. In contrast, the 1D run time commonly stays between 30 and 120 min. The two columns may be located in one oven or the second column may be in a second one. A second oven provides higher flexibility regarding temperature control. Heating rate in the first column is usually low ($1\text{--}5^\circ\text{C min}^{-1}$) in order to provide at a reasonable amount of modulations per 1D peak aiming to maintain the separations achieved in 1D . For example, if peak width is 18 s (1w_b), an appropriate P_M should not be higher than 6 s [23, 26]. Peak widths in the second dimension (2w_b) range from 50 to 600 ms, and detection requires a frequency of acquisition from a minimum of 50–100 Hz [19, 28, 29]. Several detectors meet these requirements, and mass spectrometric detectors are especially appropriate to be used with $GC \times GC$, as they provide information on the identity of separated components. However, several selective detectors have also been employed with $GC \times GC$, and the interested reader can find review papers that deal with this subject [30].

Figure 2 illustrates the whole $GC \times GC$ process steps. The result of the analysis is a great number of short chromatograms obtained from the 2D continuous analyses (step 1. Modulation). A large peak representing a co-elution of three components is presented to exemplify the

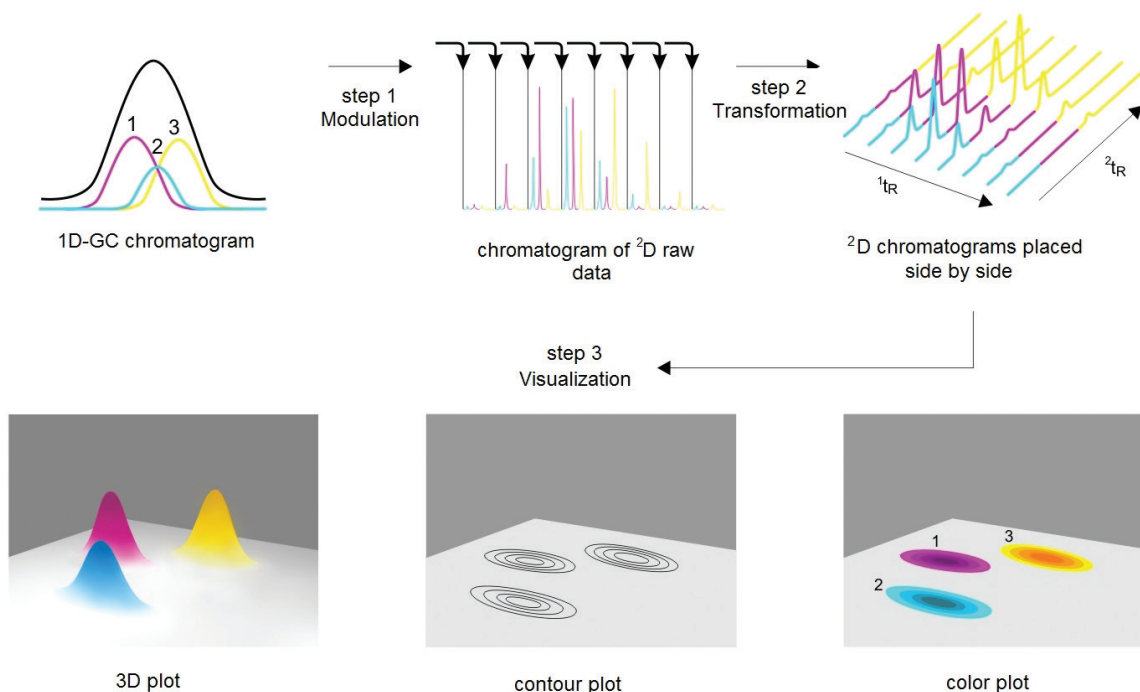


Figure 2. Representative scheme of the process of data generation and visualization of $GC \times GC$ chromatograms (basis for this figure is Dallüge et al. [31]).

modulation process. A raw chromatogram is obtained as the sum of all 2D chromatograms. Each color line represents one chromatographic peak (pink, blue, and yellow, respectively). The transformation of the raw data in a two-dimensional (2D) chromatogram (1t_R vs. 2t_R) is performed via software (step 2. Transformation). In addition, three-dimensional (3D) chromatograms are also obtained, associating raw data, the start of modulation process, $P_{M'}$ injection time, and the signals given through the detector. In the third step (Visualization) shown in **Figure 2**, a 3D-plot is presented, and the intensity of the colors represents the intensity of peak signals. A projection of the top view of the 3D-plot gives rise to 2D-plots on the plane, such as color plots. In contour plots, each line represents a different and specific intensity of the chromatographic signal.

Some advantages of the use of GC \times GC in relation to 1D-GC and GC-GC should be mentioned [32]:

- (a) Higher peak capacity, which provides better chromatographic separation among analytes and among analytes and matrix interferences.
- (b) Enhancement in detectability because of narrower chromatographic bands coming from the modulation process.
- (c) All sample are submitted to both separation processes.
- (d) Analysis time to complete both separations is the same as the one used for 1D separation.
- (e) Ordered elution of structurally related compounds may help increasing reliability of the identification process, and fingerprint provided by chromatograms may be used for pattern recognition.
- (f) Two sets of retention data also increase reliability in compound identification process.

The concept of peak capacity was introduced by Giddings in 1967 and is defined as the maximum number of compounds that can be placed side by side in the separation space (chromatogram), having a predetermined resolution in a certain period of retention time, according to Eq. (2) [33].

$$n_c = \frac{L}{w_b R_s} \quad (2)$$

where L is the column length, w_b is the base peak width, and R_s is resolution.

The theoretical peak capacity of a system is the sum of the individual peak capacities of each column. In the case of GC-GC, where several "cuts" (heartcuts) are made and these chromatographic fractions are lead to other (s) columns (s), the contribution of every secondary column should be summed up. Therefore, the total peak capacity of a GC-GC system will be n_{ctot} .

$$n_{ctot} \cong \sum n_{ci} = m \times \bar{n}_c \quad (3)$$

where n_{ci} represents peak capacity of each individual column, m is the number of columns employed, and \bar{n} is the mean peak capacity of the columns.

In a GC × GC system, theoretical peak capacity is approximately the product of the peak capacities of the individual columns:

$$n_{\text{tot}} \cong n_{\text{cD}} \times n_{\text{cD}} \quad (4)$$

Figure 3 represents the peak capacities of one chromatographic column (**Figure 3(A)**), of a heart cut two-dimensional system (**Figure 3(B)** GC-GC) and of a comprehensive two-dimensional gas chromatography system (GC × GC) [6, 34]. This representative drawing makes it clear that the theoretical peak capacity of GC × GC is higher than the one of 1D-GC and then

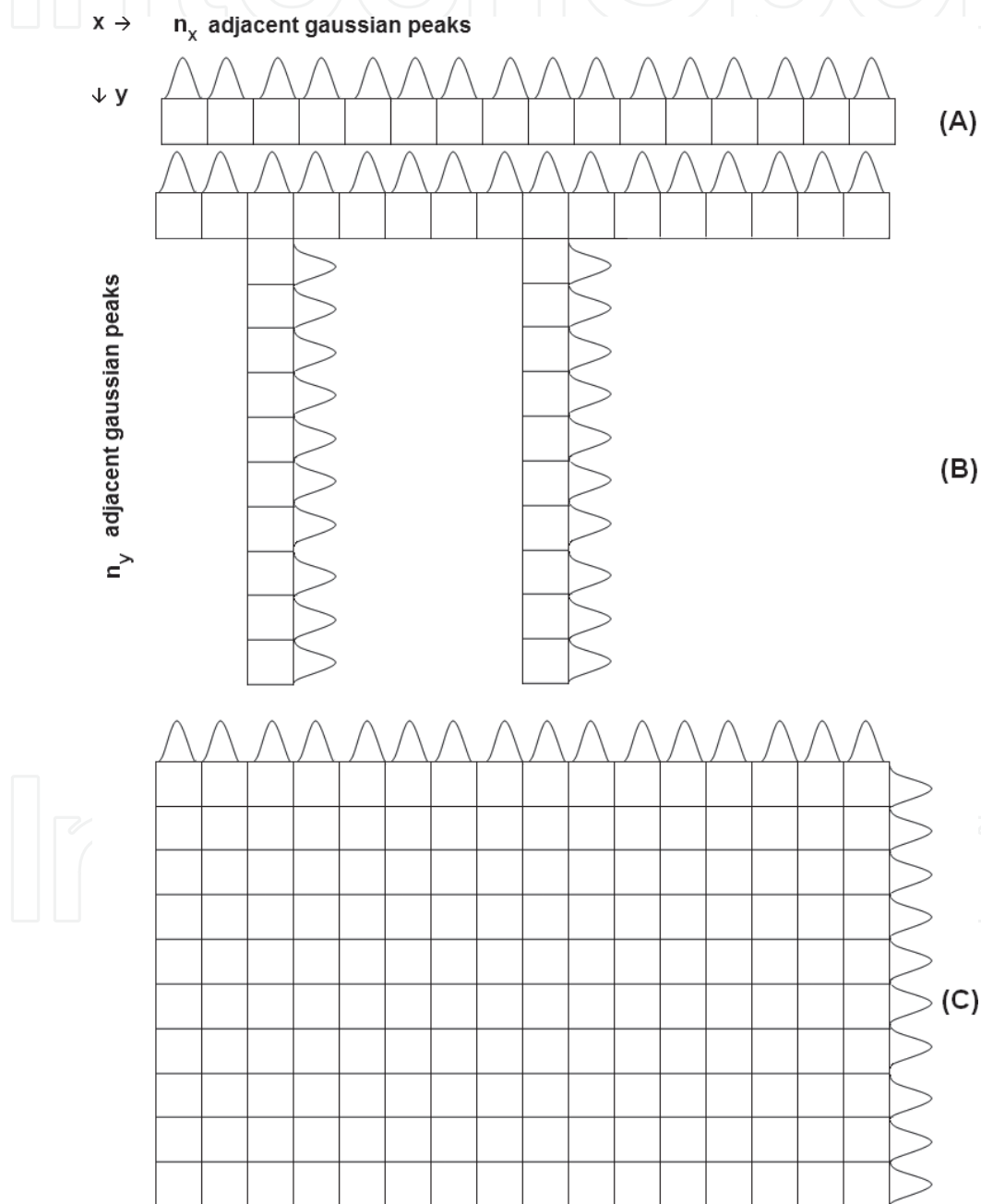


Figure 3. Representative illustration of theoretical peak capacities: (A) 1D-GC; (B) GC-GC; (C) GC × GC (based on Giddings [6]).

any other two-dimensional instrumental arrangement. However, this great peak capacity can only be achieved if there is no correlation between the separation mechanisms of the two columns, and they are considered independent of each other. In this case, the system may be called orthogonal [31]. In practice, according to statistical considerations, n_{tot} will always be lower than the maximum possible, but an appropriate choice of the stationary phases will help to take the best of GC \times GC peak capacity [35]. However, most importantly is that the dimensionalities of the sample and of the system should be combined in order to get the best, not only of the occupation of the 2D space, but also of the possible organized pattern that structurally related compounds may present. The number of independent variables that should be specified in relation to the identification of sample components refers to its dimensionality (double bonds, aromaticity, polar groups, etc.). Orderly elution in the 2D space can be obtained out of orthogonality conditions, as far as the dimensions of the sample and of the system are appropriately combined [36, 37].

3. Application of GC \times GC to the investigation of coal derived liquids

3.1. The importance of coal

Mineral coal represents an important source of energy worldwide and several aspects, such as its abundance, widespread geographical availability, storage near major centers, and ease of transportation favor its use [38]. It consists of hydrocarbons and other components that contain heteroatoms, such as nitrogen and sulfur, originated from decomposition of organic materials (trunks, roots, branches, and leaves of trees). Coal may be classified according to its maturity (carbon content and physicochemical properties) which depends on temperature and pressure conditions during its formation. The higher the carbon content the more mature the coal is considered: peat (~45%), lignite (~46–60%), sub-bituminous coal (~42–52%), bituminous coal (~46–86%), and anthracite (>86%). Among them, sub-bituminous coal is the most employed as fuel [39]. Several applications of coal may be listed, such as its use in power plants for energy generation (main use), for steel production, and cement manufacturing [40]. In addition, it is used for residential energy needs, alumina refineries, paper manufacturers, chemical and pharmaceutical industries, and for specific products, such as activated carbon, carbon fiber, and silicon metal [41].

According to the 2015 annual report of the International Energy Agency (IEA), 10 countries produce more than 100 million tons/year (Mt/y), and China leads the ranking (3527 Mt), followed by United States (813 Mt), Indonesia (691 Mt) and Australia (509 Mt). Nowadays, India has become the largest importer, while Australia is the major exporter of coal in the world [42]. However, production of coal has been decreasing in the last years, due to several reasons, such as the economic changes in China and new environmental policies all over the world. China has adopted new hydraulic, nuclear, wind and solar energy instead of coal, in many cases due to concerns about environmental effects involved in all the processes included in the coal production, its products and derivatives [43]. More than 70 pollutant compounds are generated in the combustion of coal. In addition, the polluting potential can be seen in

different stages of the process of production (mining, production itself, use, and disposal of residues) and requires investments in green technologies to minimize risks of contamination and to avoid environmental accidents [38]. The main environmental effects of coal utilization are closely linked to the type of coal and its chemical composition, such as carbon, sulfur, and nitrogen content. During combustion, carbon monoxide (CO), sulfur dioxide (SO₂), and nitrogen oxides (NO_x) are emitted, among other pollutants [44]. Due to these environmental problems, coal upgrading has been prioritized. Several different processes of coal upgrading can be performed, such as moisture removal, de-mineralization, and removal of harmful constituents (e.g., sulfur, nitrogen, and heavy metals) [45–51]. Consequently, it is important to know the composition of coal and of its derivatives in order to develop environmentally friendly processes and uses of these materials.

3.2. Coal derivatives

Liquids derived from coal are obtained mainly through pyrolysis, liquefaction, and solvent extraction. When coal is heated to high temperatures (500–1000°C) in an inert environment, 20–40% of the original solid is released into gas or volatiles. This process is called pyrolysis or devolatilization of coal. Coal is also converted into liquid fuel either directly or indirectly, via liquefaction [52]. Direct coal liquefaction, industrialized in the western countries of the past century, is considered as an effective way to produce transportation fuels and chemicals [53]. Liquefaction employs severe conditions of temperature and pressure to achieve a significant productivity. However, coal extracts may also be obtained with milder conditions, such as extraction with solvents, where compounds that are less strongly linked to the carbonaceous matrix are obtained. Solvent extraction may be performed in a relatively high temperature environment (370–480°C), where the matrix can swell with the solvent and overcome the van der Waals forces allowing the soluble material to be extracted. A nonhydrogen-donor solvent can be used, such as anthracene oil, in the absence of hydrogen [52]. Other diverse techniques may be employed for coal extraction in analytical scale, and some of them may be cited: Soxhlet extraction [54, 55], ultrasound extraction (UE) [56–58], and supercritical fluid extraction (SFE) [55, 59–61].

Coal tar is the liquid produced in pyrolysis, and it is also a byproduct of coal carbonization/gasification. It contains complex chemicals that are otherwise difficult to acquire from other fossil fuels such as gas and oil [62]. During thermal processes, several chemical reactions occur: cracking, dehydration, isomerization, rearrangements, aromatization, condensation, etc., and the amount of coal tar produced with pyrolysis is around 2.5–4% upon the weight of coal. Heavier molecular weight compounds are broken in smaller molecules under a partially or totally oxygen free atmosphere [63]. The pyrolytic oil may be employed as an alternative fuel and in fuel mixtures, and in this case, it should present properties that are similar to fossil fuels [64]. For that purpose, it is important to remove oxygen and other heteroatoms during pyrolysis [63]. In general, a wide variety of aromatic chemicals including polycyclic aromatic hydrocarbons (PAH), phenols, and heterocyclic compounds (containing sulfur and nitrogen atoms) exist in coal tar, depending on the reaction temperature and the nature of original coals [62]. Its complex compositions make coal tars an important feedstock for value-added substances and materials [65], although its content in carcinogenic compounds is a concern [66].

Quinolines and derivatives are important constituents of pharmacologically active synthetic compounds and have been applied for the treatment of malaria [67], HIV [68] and as corrosion inhibitors for steel [68]. Antitumor, antibacterial, anti-inflammatory, psychotropic and anti-histaminic properties have been attributed to many alkaloids, whose structures are based on carbazoles [69].

Pyridine is widely employed as starting material to produce agrochemicals, as, for example, paraquat and diquat, chlorpyrifos, and antifungal agents such as the zinc salt of pyrimethion and pharmaceuticals. It is also used as solvent in organic chemistry along with methyl-pyridines [70]. Carbazoles have also been used as photoconductors, semiconductors, and, due to their light-emitting properties, they are interesting organic tools for physics experiments [69, 71]. Approximately 100% of the carbazole, quinoline and thiophene compounds are derived from coal tar [64].

Therefore, an environmentally friendly use of coal tar demands evaluation of its molecular features. A deep and wide characterization of physicochemical and molecular characteristics of coal and coal tars is fundamental to clarify their complex composition. An appropriate analytical approach helps to improve coal processing in order to obtain higher added value products, as well as enlighten the possible environmental impacts of coal (or coal tar) during combustion, pyrolysis and other industrial processes [64, 65].

3.3. Characterization of coal tar

Characterization of coal is usually made through the analyses of the liquids that are derived from coal using extraction, pyrolysis, and liquefactions. Several research works have been published on this matter, dealing with molecular mass distribution and characterization of molecular structure of coal liquid derivatives. Molecular weight and functional groups distributions are carried out by size exclusion chromatography [72] and Fourier transform infrared spectroscopy (FTIR) [73], respectively. The ratio of aromatic/saturated compounds and the distribution of heteroatoms has been determined by X-ray photoelectron spectroscopy (XPS) [74], magnetic resonance spectroscopy (NMR) [75], and X-ray absorption spectroscopy (XAS) [76]. Although these analytical techniques provide satisfactory information about coal tar characterization, analyses in molecular level are still a challenge.

Extracts of liquefaction and coal tar were analyzed by laser desorption (LD)-MS and matrix-assisted laser desorption/ionization (MALDI)-MS for the determination of the molecular mass (MM) distribution, and results were compared to size exclusion chromatography (SEC) [77]. In the SEC, the MM distribution of the coal tars with a carbon content of up to 89% was almost identical and tending to decrease for higher rank coals. For coal-derived liquefaction extracts up to 87% carbon, there is a constant increase in MM with increasing rank and a steady decline for coals with more than 87% of carbon. Analyzes carried out with MALDI showed that liquefaction extracts were similar among them, with a little increase in MM with the elevation of the carbon content; however, coal tar contained a higher MM distribution. SEC has been shown to underestimate the MM range when compared to (MALDI)-MS results.

Zhu et al. developed MS analytical methods using gas chromatography/mass spectrometry (GC/MS), time-of-flight MS coupled with an atmospheric solids analysis probe (ASAP-TOFMS)

and electrospray ionization (ESI)-Orbitrap MS for the characterization of a petroleum ether (designated as PE-HTCT) of a high-temperature coal tar (HTCT) [66]. GC/MS detected hydrocarbons and molecules with low molecular weight and polarity, while mid-polarity compounds were investigated by PE-HTCT, without any sample pretreatment, through a rapid *in-situ* ASAP-TOFMS analysis. (ESI) Orbitrap MS was employed to characterize heteroatom-containing compounds of PE-HTCT. The combination of the three MS-based analytical methods provided an overview of the components present in the PE-HTCT. Sixty-seven percent of the species identified on PE-HTCT using GC/MS were hydrocarbons, but ASAP-TOFMS and ESI-Orbitrap MS detected only a small portion of them. These two analytical techniques were better choices for identification of polar compounds and heteroatom-containing compounds.

Gas chromatography with mass spectrometric detection (GC/MS) is commonly employed for the analysis of volatile fractions of liquids derived from coal [65, 66, 78–82] including also the use of an analytical pyrolyzer as injector [83]. However, other detectors are also employed, such as flame ionization detector (FID) [84–86] and atomic emission detector (AED) [87].

There are a considerable number of published research papers that report the occurrence of complex mixtures of organic compounds in coal tar. Major compounds are polycyclic aromatic hydrocarbons (PAH), and heterocyclic compounds containing oxygen, nitrogen, and sulfur are present as minor constituents [64]. Even though one-dimensional gas chromatography (1D-GC) is a well-established analytical technique for the analysis of coal tar, it presents drawbacks because the matrix is extremely complex, containing a high number of compounds, which result in an unresolved complex mixtures in many cases. Compounds present in higher amounts are together with trace level compounds (such as sulfur compounds) that are important in terms of health, environment, and process, which makes the analysis of such target trace compounds an extremely difficult task [63, 88]. Due to the already reported advantages of GC \times GC, it is the technique of choice for the analysis of coal tar. However, in comparison with reports on bio-oil from biomass, the ones published on this matter are scarce [63, 89–92].

3.4. Application of GC \times GC to liquids derived from coal

Researchers have highlighted the advantages of GC \times GC for the analysis of coal-derived liquids, especially the possibility of resolving hundreds of compounds, in comparison with 1D-GC. The advantage of a mass spectrometric detector coupled to GC \times GC, the structured elution order of structurally related compounds and the information about two sets of retention data also help identifying unknown compounds.

The parallel between pyrolytic oils from biomass (bio-oil) and coal (coal tar) can be seen in their complex composition as coal tar contains linear and branched saturated hydrocarbons, aromatic hydrocarbons and several compounds containing heteroatoms as well as bio-oils. Characterization of liquids from coal liquefaction has been mainly performed by GC \times GC/TOFMS [92–94]. Applications of GC \times GC/TOFMS to coal tar are also reported, such as, the use of chemical signatures of coal tars of different manufacture gas plants (MGP), where coal tar is a byproduct [90]. Coal tar is a common occurrence at MGP sites, some of which are severely affected and environmental remediation of polluted sites is a major challenge

[95–98]. A GC \times GC method provided minimal sample pretreatment and a highly accurate and detailed chemical signature [89, 93]. The analytical method developed specifically for coal tar was different from the methods already reported for conventional forensic analysis of oil-spill in scientific literature [89, 99] and nitrogen containing compounds in coal tar, which are minor components of this matrix [91]. Some examples are given in the following texts.

3.4.1. Sulfur compounds in bitumen and tar

The removal of organic sulfur compounds (OSC) from coal is essential to provide an environmentally acceptable use for coal. Combustion of sulfur compounds leads to the emission of SO_x gases, which are major contributors to acid rain [100]. In addition, OSC promote equipment corrosion [101] and can be deleterious to human health, contributing to respiratory diseases, such as emphysema, pneumoconiosis, asthma, and bronchitis [102]. It is also well known that organically bonded sulfur is difficult to remove from coal with the available technology. Development of new technological approaches for coal desulfurization depends on knowledge about the different organic sulfur compounds present in coals. Extraction of organic compounds from coal may be performed through a variety of processes, and among them, pyrolysis is considered as one of the most efficient thermal treatments in terms of yield of extracted material [99]. Pyrolysis causes breakage and rearrangement of several chemical bonds, generating artifacts. Conversely, process such as extraction is softer, and in this case, only compounds weakly bonded to the carbonaceous matrix are extracted. Bitumen is the name given to a coal extract. If the objective is to identify the compounds that are originally present in coal matrix, extraction processes are an appropriate choice. Several techniques of extraction may be employed to obtain bitumen, such as Soxhlet extraction, ultrasonic extraction (UE), and supercritical-fluid extraction (SFE) [100, 102].

Selective sulfur detectors have been used for the analyses of OSC in several matrices (petroleum and derivatives, coal tar and pitch, garlic, wine and beer volatiles, etc), as they reduce analysis time by eliminating cumbersome and time-consuming sample preparation procedures that can cause contamination or loss of analytes. A review about this subject has been reported by Wardencki and Zygmunt [103]. Among them, some may be listed: flame-selective flame detector and (FPD), double flame FPD [103], photometric detector of (PFPD) [104], sulfur chemiluminescence detector (SCD) [103, 105], and the atomic emission detector (AED) [106]. On the other hand, these detectors also present some drawbacks, as the lack of structural information, the quenching effect due to co-elution with hydrocarbons, water or CO₂ for FPD, among others. As far as the authors are aware, there is no paper reported for the analysis of OSC via GC \times GC with a sulfur selective detector, although an analytical method has been developed for diesel samples and used to quantify sulfur impurities in petroleum fractions, which are also complex samples.

Machado et al. [99] employed three different techniques of extraction (ASE, UE, and SFE) to obtain bitumen from coal. The largest number of compounds (3347) was obtained through ASE, while extracts were analyzed by GC \times GC/TOFMS. The analyses made by 1D-GC/qMS in scan mode resulted in 93 tentatively identified compounds, although none of the target OSC could be identified (**Figure 4A**). The following classes of OSC were found: thiophenes, benzothiophenes, naphthothiophenes, dibenzothiophenes, benzonaphthothiophenes, and

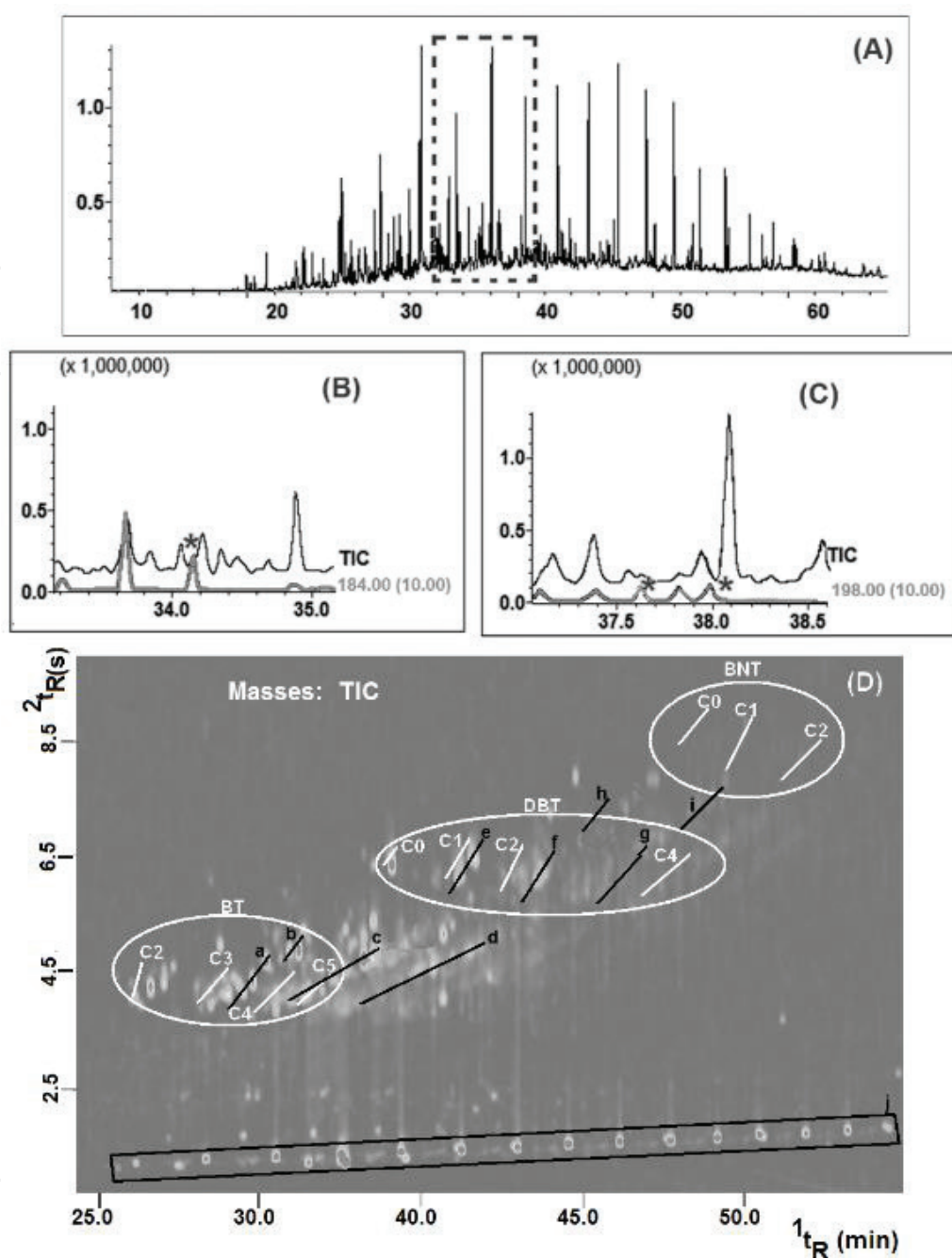


Figure 4. 1D-GC/qMS of the ASE bitumen: (A) scan mode; (B) EIM mode, with m/z 184 as the chosen ion (bellow line); (C) EIM mode, with m/z 198 as the chosen ion (bellow line). (D) GC \times GC/TOFMS color plot of ASE bitumen. White lines - sulfur compounds: benzothiophenes (BT), dibenzothiophenes (DBT), benzonaphthothiophenes (BNT); number of methyl groups attached to compounds (CX). Black lines – hydrocarbons: a, naphthalenes with three methyl groups; b, *H*-xanthenes; c, naphthalenes with four methyl groups; d, naphthalenes with five methyl groups; e, phenanthrenes with one methyl group; f, phenanthrenes with two methyl groups; g, phenanthrenes with three methyl groups; h, pyrenes with one methyl group; i, pyrenes with two methyl groups; j, aliphatic hydrocarbons;. (adapted from Machado et al. [99]).

thioxanthenes, reaching 150 OSC. **Figure 4A** illustrates the image pattern formed by the peaks in the two-dimensional separation space (2D), which is an important characteristic of 2D-chromatograms that enhances the reliability of the compound identification process,

as their distribution in the chromatogram is due to their physicochemical characteristics. Molecules are separated according to their number of carbon atoms, and this phenomenon is known as roof tile effect. Examples of roof tile effect are common in 2D-chromatograms of petroleum and petroleum-derived samples [17] and were also observed in coal bitumen.

The use of extracted ion-monitoring tool (EIM) made it possible to identify six alkylated and nonalkylated dibenzothiophenes (DBT). Co-elutions of polycyclic aromatic sulfur heterocycles (PASH) with polycyclic aromatic hydrocarbons (PAH) are well reported in scientific literature due to the occurrence of the same ions in their mass spectra and are clearly shown in the following examples. A dashed red line shows one region of the chromatogram where some compounds elute (**Figure 4A**) and the asterisks mark the chromatographic peaks under discussion in **Figure 4B** and **C**: peaks corresponding to m/z 184 (DBT or naphthothiophenes, NT) and m/z 198 (C1-DBT), respectively, where C1 designates one alkyl group with one carbon atom. The peak corresponding to ion 184 (**Figure 4B**, pink line) was observed in scan mode (**Figure 4B**, black line), as a frontal shoulder of major intensity and was identified as phenyl ethyl ether (retention time 34.2 min). The earlier eluting peak that contains the same characteristic ion does not correspond to an OSC, but to methylnaphthalene. However, a careful look in the GC \times GC/TOFMS shows that an OSC elutes in this same region and that the sole use of EIM of 1D-GC/qMS may lead to erroneous results, such as misidentification, where OSC remains unnoticed. A further consequence of co-elutions is the overestimation of a PAH (or a matrix interferent peak) that co-elutes with an OSC leading to error in quantitative analysis. It is important to highlight that both chemical classes (PAH and PASH) are toxic. In some cases, PASH may even show higher mutagenicity than PAH. This is the case of the mutagenicity of 2- and 3-aminodibenzothiophene is higher than the one of benzo[*a*]pyrene [107]

An alternative to get around this analytical problem is to submit the sample to pre-separation steps, in order to minimize the presence of interferents. However, every time new stages are added to an analytical procedure, higher probability of contamination and loss of analytes are also added. Consequently, the analytical method becomes longer. The adoption of direct injection of the sample in a GC \times GC/TOFMS or the use of a simple pretreatment step before its chromatographic analysis seem to be more appropriate, as it eliminates the already mentioned analytical drawbacks. In a similar way, **Figure 1C** presents two out of the four possible C1-DBT isomers that were identified (two asterisks indicate the t_R of each one of them) and the co-elution of the major peak of methyl anthracene (C1-anthracene, t_R 38.0 min, asterisk more to the right) with a methyl-dibenzothiophene (C1-DBT). The blue line shows the m/z 198 (EIM), and the black line designates the current derived from all detected ions (scan mode).

OSC in coal tar were also investigated, and 1D-GC co-elutions of PASH with PAH and phenols were also elucidated in GC \times GC/TOFMS analyses [89]. Some of them were reported for the first time, such as the co-elution of trimethyl thiophene and phenol. The co-elution of C4-BT and trimethyl-naphthalene in coal tar and the separation of these compounds by GC \times GC/TOFMS served as an illustration of many other co-elutions. In addition, thioxanthene was tentatively identified for the first time in coal tar, and the quality of mass spectra of compounds was noticeably enhanced with GC \times GC/TOFMS in comparison with 1D-GC/qMS.

3.4.2. Nitrogen containing compounds in coal tar

The determination of the forms of nitrogen in coal is attracting increasing attention because of attempts to identify relationships between fuel nitrogen functionality and NO_x production in coal combustion. Previous interest in nitrogen functionality in coals had arisen from efforts to understand the chemical transformations occurring during coal coking [108]. Nitrogen polyaromatic compounds (NPAC) are present in fossil fuels as a complex mixture. Percentages of NPAC are usually less than 0.5% in crude oil and around 1–2% in shale oil and coal tar [49]. While conventional petroleum-derived fuels are low in nitrogen, typical liquid fuels derived from coal have much higher nitrogen contents and give rise to significant amounts of NO, during combustion. The conversion of nitrogen (1% or more) from coal to NO, even at low combustion temperatures, is a serious environmental problem [109]. Over the past few years, it has been recognized that many of the nitrogen-containing compounds found in coal-derived liquids are both carcinogenic and mutagenic, particularly in the presence of other polycyclic aromatic compounds (PAC). Several basic nitrogen compounds are toxic and the aza-heterocycles and primary aromatic amines are suspected of carcinogenic activity. In general, neutral nitrogen compounds are supposed to be less toxic; however, several some dibenzocarbazoles have been already reported as carcinogens [49]. In addition, the combustion of nitrogen rich fuels is known to release many NPAC and NO, into the atmosphere [110]. Nitrogen-containing compounds play an important role in linking sub-units of the macromolecular coal structure through hydrogen bonding and N-linkages. Consequently, analysis of these compounds in liquids derived from coal is important as nitrogen-containing compounds are known to deactivate catalysts usually employed in the upgrading of primary products of coal liquefaction [74].

The N-containing compounds can be classified in neutral pyrrolic and basic pyridinic types, according to their chemical characteristics. The neutral nitrogen species comprise carbazole, pyrrole, indole, and their alkylated and benzo analogues; while basic nitrogen species include pyridines, quinolines, benzoquinolines and their alkylated analogues [30, 110]. N-compounds occur as minor components in coal tar, mainly as pyridinic, pyrrolic, and some aromatic primary amines [111].

Gas chromatography coupled to different selective detectors, such as the chemiluminescence detector (NCD), has been used for the analysis of NPAC in bituminous coal [112]. Burchill et al. used nitrogen and phosphorus detector (NPD) for the analysis of NPAC in coal tar products [49, 113]. The hyphenation of GC × GC with nitrogen chemiluminescence detection (GC × GC-NCD) has been reported to achieve the identification of various N-compounds in diesel fuel [114–116], while NPD was employed for the analysis of N-containing compounds in heavy gas oil [30]. To date, the use of GC × GC with selective detector for the analysis of nitrogenous compounds in coal tar has not been reported.

Nitrogen detection is subject to interference with the hydrocarbons of the matrix [91]. Therefore, different techniques of isolation of N-compounds from coal tar are traditionally carried out by aqueous acid extraction [49, 50] precipitation with gaseous hydrogen chloride [117], solvent extraction with methanol [118], and cation-exchange chromatography [119, 120].

Informative detectors, such as the most commonly used mass spectrometers (quadrupole, ion trap), are not sensitive enough to achieve detection of N-compounds at low concentrations. Moreover, they do not provide selective unambiguous extraction, identification and quantification of N-compounds in complex matrices such as coal tar. Speciation of NPAC in coal tar by GC \times GC has already been reported in the literature using time-of-flight mass spectrometry detector (TOFMS). Silva et al. [91] applied GC \times GC/TOFMS to determine NPAC in a Brazilian sub-bituminous coal tar without any previous prefractionation. One hundred and twelve NPAC were tentatively identified, and twelve NPAC were identified through injection with analytical standards. Pyridines and quinolines were the major basic N-compounds, whereas carbazoles were the major neutral ones. An important contribution of the GC \times GC was the identification of all possible isomers of methyl quinolines, methyl pyridines and methyl carbazoles, being seven, three and five compounds, respectively. In addition, it was possible to identify nitriles, which is a very difficult task to perform using direct injection in GC/MS, as they are present in trace levels [121] 1D-GC offers poor separation between neutral and basic NPAC, mainly for the pairs acridine/carbazole and indole/quinoline, which cannot be resolved by mass detectors such as quadrupole, and ion trap [114]. However, the identification of these compounds was achieved with GC \times GC/TOFMS due to differences in the second dimension retention time and with the help of spectral deconvolution.

Chromatographic separation of basic N-compounds is still also a challenge because pyridines, anilines, quinolines and acridines overlap in the first dimension [116]. Therefore, a preliminary fractionation of hydrocarbons, oxygen, nitrogen, and sulfur compounds must be performed in order to provide greater sensitivity and resolution, whenever one-dimensional techniques are employed. However, the separation of these classes has been achieved with no pretreatment, but with direct analysis with GC \times GC/TOFMS, as presented in **Figure 5** [91]. The separation of quinolines from polyaromatic hydrocarbons and anilines from phenols is another challenge, which is exemplified in **Figure 5**.

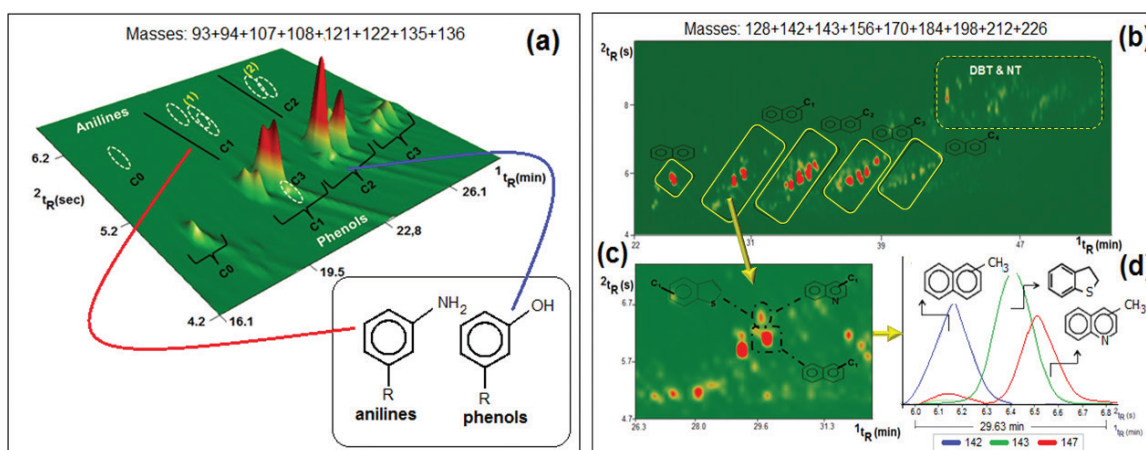


Figure 5. Demonstration of the peak capacity and resolution of the GC \times GC/TOFMS: (a) 3D-Diagram (EIM mode) from selected region of anilines (C0–C3) and phenols (C0–C3); (b) 2D-Diagram (EIM mode) highlighting the region of elutions of alkyl naphthalenes (N), dibenzothiophenes (DBT) and naphthothiophenes (NT); (c) detail of the diagram showing the separation of three compounds and (d) reconstructed chromatogram with the specific ions of each of the three compounds shown in (b), including their structures (adapted from Silva et al. [91]).

Extrography is one of the methods of sample preparation used in literature [121] that allows separation among aliphatics, aromatics and neutral NPAC, whereas all phenols still elute in the fraction containing the basic NPAC. However, **Figure 5(a)** shows that it was possible to adequately separate phenols from anilines (basic compounds) in the second dimension of GC \times GC. **Figure 5(b)** also clearly presents the roof tile effect related to alkyl naphthalenes (N), dibenzothiophenes (DBT) and naphthothiophenes (NT), as well as the separation between an aromatic hydrocarbon and two other compounds in the second dimension (2D) (one PAH and one PASH), although co-elution of PAH, PASH and NPAC compounds is evident (**Figure 5(c) and (d)**). In this case, detection and tentative identification of the three co-eluting compounds was possible due to spectral deconvolution (**Figure 5(d)**).

4. Application of GC \times GC to the investigation of pyrolytic liquids from biomass

4.1. The importance of biomass and bio-oil

Environmental problems fueled by the combustion of fossil fuels, the future decline in oil production due to the depletion of reserves, as a precursor of fossil fuels biomass is composed of carbon and can be an alternative to the substitution or complementation of fossil fuels with many applications [122].

Biomass can be used in energy applications for the production of heat and transport fuels. The conversion of biomass into fuels and chemicals, such as bio-plastics, biofertilizers and bio-polyesters, can share the demand with those of petrochemical origin, avoiding the depletion of fossil reserves in several regions of the world. A valorization of the entire content of biomass in bio refineries inspired by the model of those exploited for petroleum products constitutes one of the key issues [122–124].

Biomass is a renewable source of energy that could mitigate pollution of fossil fuels. It is abundant as agricultural residues and forest waste, whose thermochemical decomposition, under optimal conditions produces valuable gases, condensates and char. Char is used in fertilizers, while the condensed liquid, pyrolysis oil or bio-oil, serves as the mother liquor for numerous value-added chemicals and prospective engine-fuel applications [122]. Bio-oils are complex mixtures of water and hundreds of organic compounds that belong to different chemical classes, such as acids, aldehydes, ketones, alcohols, esters, anhydro-sugars (such as levoglucosan), furans, phenols, guaiacols, syringols, nitrogen-containing compounds, as well as large molecular oligomers (holocellulose-derived anhydro-oligosaccharides and lignin-derived oligomers [125–128]. Bio-oil compounds may be used for several different applications, such as phenolic compounds as raw material in chemical industries for the production of phenolic resins, among other uses [122]. Benzenediols such as catechol and hydroquinone have many applications as antiviral and as antioxidant for the production of rubbers, inhibitor of vinyl polymerization reactions, and also in topical application in skin whitening [123, 124, 129]. Guaiacol can be used as an indicator in several experiments involving enzymes, due to its characteristic color change according to reaction medium. In addition, it has been also applied

as antiseptic, expectorant, and anesthetic [130]. Furthermore, ketones are applied in chemical syntheses, as, for example, furanones are precursors in the synthesis of brominated derivative fungicidal coatings and are currently obtained only by extraction of marine algae [131, 132].

4.2. Application of GC \times GC to pyrolytic liquids derived from biomass

Chemical analysis and complete characterization are absolutely essential to gather the necessary data that provide information for research into bio-oil. The chemicals encountered in bio-oil depend on the composition of biomass, from which it is produced, as well as on the process parameters used during pyrolysis. Investigation of the molecular composition of bio-oil is mandatory for ensuring its proper characterization and for determining applications for which it is appropriate [125–127]. Considering the great variety of biomasses that can be used in the pyrolysis process, as well as the high complexity of bio-oils, due to the large number of components and chemical classes present, the characterization of different bio-oils, as well as their differentiation, presents itself as an analytical challenge [125, 126]. Kanaujia et al. [127] reviewed the most used analytical techniques to characterize the bio-oils of which we can mention liquid chromatography (LC), gel permeation chromatography (GPC), infrared spectroscopy (IR), GC, among others that were addressed according to their corresponding technical characteristics. GC/MS is an important tool to evaluate bio-oil profiles, helping to determine its subsequent final use, as well as for monitoring upgrade processes.

Hyphenated techniques such as heart-cutting multidimensional GC (MDGC) [133] and comprehensive two-dimensional gas chromatography (GC \times GC) have gained much attention for the analysis of bio-oils in the last years [134–136]. GC \times GC coupled to mass spectrometry (MS) proved to be a powerful technique for the separation of complex matrices and is ideal for characterizing compounds with similar chemical structures [137–139]. Similarly to what has been seen for the complex liquids derived from coal, one of the main advantages of GC \times GC is an enormous increase in the resolving power when compared to 1D-GC [140]. Additionally, different well-ordered groups that are characterized by distinct patterns can be distinguished in the two-dimensional plane, providing important information about the chemical structures of the molecules of interest [134, 135].

The first studies that employed GC \times GC for the analysis of bio-oils were conducted by Marsman and Sfetsas. Marsman et al. [141–143] used GC \times GC-FID and GC \times GC/TOFMS systems to tentatively identify roughly 248 and 368 compounds in bio-oil from beech (*Fagussylvatica*) and hydrodeoxygenated beech bio-oil (using ruthenium as catalyst), respectively. The authors also classified the compounds according to their chemical function into nine groups (acids, aldehydes, ketones, furans, guaiacols, syringols, sugars, alkyl phenols, alkyl-benzenes). The major compounds found in beech bio-oil were: hydroxymethyl furfural, furanone, furfural, mequinol and butanediol. Sfetsas et al. [144] have also analyzed the constituents of three bio-oils, where GC \times GC was employed with FID and TOFMS detection systems. In this study, approximately 96 compounds (area >0.3%) were tentatively identified, and they were classified as acids, esters, aldehydes, ketones, hydrocarbons, aromatic hydrocarbons, phenols, sugars, and other nonclassified compounds. The major components were acetic acid, levoglucosane, and hydroxypropanone. Several other researchers have also reported the composition of different bio-oils.

Moraes et al. have used GC \times GC for the qualitative characterization of bio-oils derived from the intermediate pyrolysis of various agro industrial residues such as orange bagasse [145], peach pit [146, 147], rice husk [147], and sugar cane straw [135]. Analysis of bio-oil from orange bagasse [145] was performed, without any pretreatment, by GC \times GC-FID and GC \times GC/TOFMS. A hundred sixty-seven compounds from different chemical classes (acids, aldehydes, ketones, phenols, esters, ethers and some nitrogen-compounds) were tentatively identified, and only twenty-six among them presented a chromatographic area percentage above 1%. Another research work of the same research group has shown the presence of approximately 500 compounds detected in each one of the bio-oils from peach core and rice husk. A conventional set of columns was employed in GC \times GC/TOFMS, and the major part of compounds were ketones, phenols, alcohols, ethers, acids, aldehydes sugar derivatives and hydrocarbons [147].

Migliorini et al. [146] performed a comparative study between GC/qMS and GC \times GC/TOFMS for peach pit bio-oil. The results showed 51 and 220 tentatively identified components, respectively, confirming the superiority of the multidimensional technique. The ordered distribution of the compounds in the 2D space allowed the identification of all the isomers of C1 to C4 alkyl phenols. Compounds such as alcohols, aldehydes, anhydrides, ketones, esters, ethers and phenols were present in the chromatograms of the two analytical systems employed, whereas phenols shared the major chromatographic area percent. However, GC \times GC/TOFMS provided tentative identification of carboxylic acids, hydrocarbons and sugar derivatives such as levoglucosan that were not found in 1D-GC/MS analyses.

Moraes et al. [147] studied the similarities and differences between peach pit and rice husk bio-oils, using GC \times GC/TOFMS with a conventional set of columns. The results showed similar qualitative and semi-quantitative composition for both bio-oil samples, with the presence of ketones, phenols, alcohols, ethers, acids, sugar derivatives, aldehydes and hydrocarbons. A hundred and six and 223 compounds were tentatively identified in rice husk and peach pit bio-oils, respectively. The bio-oil of sugar cane straw was also investigated using a similar analytical approach. Furfural and hexenoic acid were major compounds in this bio-oil, and a total of 123 compounds were tentatively identified.

Araújo et al. [148] evaluated volatile organic compounds that were released from biopitch (obtained via the distillation of *Eucalyptus* sp. bio-oil) and its polyurethane films. Biopitch was used in place of polyols in the polyurethane synthesis. The chemical characterization was performed in a system using solid phase microextraction (SPME) and GC \times GC/TOFMS. Although these researchers had the expectation of finding aromatic compounds in the heavier fraction of *Eucalyptus* biopitch, they verified the presence of phenols with an aromatic ring, which differentiates this biopitch from those obtained from fossil materials (coal and oil). These results have shown that the *Eucalyptus* biopitch has potential for the development of “green” materials.

Mango seed waste represents an important environmental problem in Brazil due to the large amounts produced in the industrial processing of the corresponding fruit. Pyrolysis is an attractive alternative for the use of the residual seeds. Lazzari et al. [149] have investigated the pyrolytic liquid of mango seed waste (tegument and almond) using GC \times GC/TOFMS. More than 100 compounds were tentatively identified in each bio-oil, through comparison of experimental and reported linear temperature programmed retention indices (LTPRI) and

mass spectra. Major chemical classes in terms of chromatographic area percentage were ketones (20.6%), acids (16.8%), and hydrocarbons (7.2%) in the almond bio-oil, while the bio-oil of the tegument was rich in phenols (32.6%) and ketones (22.9%).

Almeida et al. [150] reported qualitative and semi-quantitative characterization of bio-oil generated from the residual fiber obtained from the shells of coconut (*Cocos nucifera* L. var. Dwarf). Chemical characterization of the bio-oil and the aqueous phase was performed by GC/qMS and GC \times GC/TOFMS. Forty-two compounds were identified in the organic extract of the aqueous phase and 81 in the bio-oil, using GC/qMS, while GC \times GC/TOFMS provided identification of 68 and 95 for the same samples, respectively. Alkyl phenols were predominant in both phases, and aldehydes, ketones, and phenols were also present in both pyrolytic products. The chromatographic area percent of phenols in bio-oil was 59 and 12% for aldehydes (mainly furfural), using GC/qMS, while aqueous phase extract rendered 77% for phenols. The composition of pyrolytic bio-oil and aqueous phase from shells of coconut indicates that these products may find potential use in industry, which also means that environmental impact due to wrong disposal of coconut shells may also be minimized.

The vegetable oil (VO) from the seeds and the bio-oil (BO) from the pyrolysis of the residual cakes from *Crambe abyssinica* were characterized with GC/qMS and GC \times GC/TOFMS by Onorevoli et al. [151]. Three residual cakes were pyrolyzed: one coming from mechanical pressing extraction, another from Soxhlet and a third from the compressed propane extraction (CPE, subcritical state). Procedures resulted in the identification of 195, 307, and 361 compounds, respectively, in the bio-oils of residual cakes. While the BO presented complex composition, with esters, ketones, ethers, phenols, alcohols, acids, hydrocarbons, and nitrogen compounds, VO were basically composed of fatty acids, mainly erucic and oleic acid.

The amount of nitrogen compounds was higher in GC \times GC/MS analysis than in GC/MS, and several co-elutions were found in 1D-GC that may explain the incorrect identification of the nitrogen containing analytes, which explains this difference. **Figure 6** shows one illustrative example through the separation of heptenoic acid, *p*-cresol and C_2 -aniline, which were identified in the CPE bio-oil sample by GC \times GC/TOFMS ($t_R = 15.30$ min and $^2t_R = 3.74$ s, 4.76 and 4.80 s, respectively). *P*-cresol was the only one compound identified by GC/MS in this corresponding retention time, with a chromatographic area percent of 12.0%. This example shows that a direct analysis of this bio-oil by GC/MS, without previous fractionation steps can lead to erroneous results due to co-elutions.

The castor seed cake is a solid residue generated from castor oil extraction during the pressing of castor seeds. In 2011, world production of castor seed was 2,767,548 tons [3], generating approximately 1,383,774 ton of waste. Based on this fact, Silva et al. [152] used slow pyrolysis from castor seed cakes to obtain bio-oil and determine its chemical composition by GC \times GC/TOFMS. The calorific value of the castor bio-oil was found to be 37.5 MJ kg⁻¹, similar to that of petroleum-derived fuels (43–46 MJ kg⁻¹). In addition, a large variety of compounds have been tentatively identified in this bio-oil, such as hydrocarbons (paraffins, olefins and aromatics), nitrogen compounds (nitriles, anilines, quinolines, pyridine, indoles, pyrazines, pyrroles, carbazols and acridines), oxygen compounds (phenols, acids, ketones, esters, and furans) and sulfur compounds (disulfides and thiophenes), in a total of 408 tentatively identified compounds.

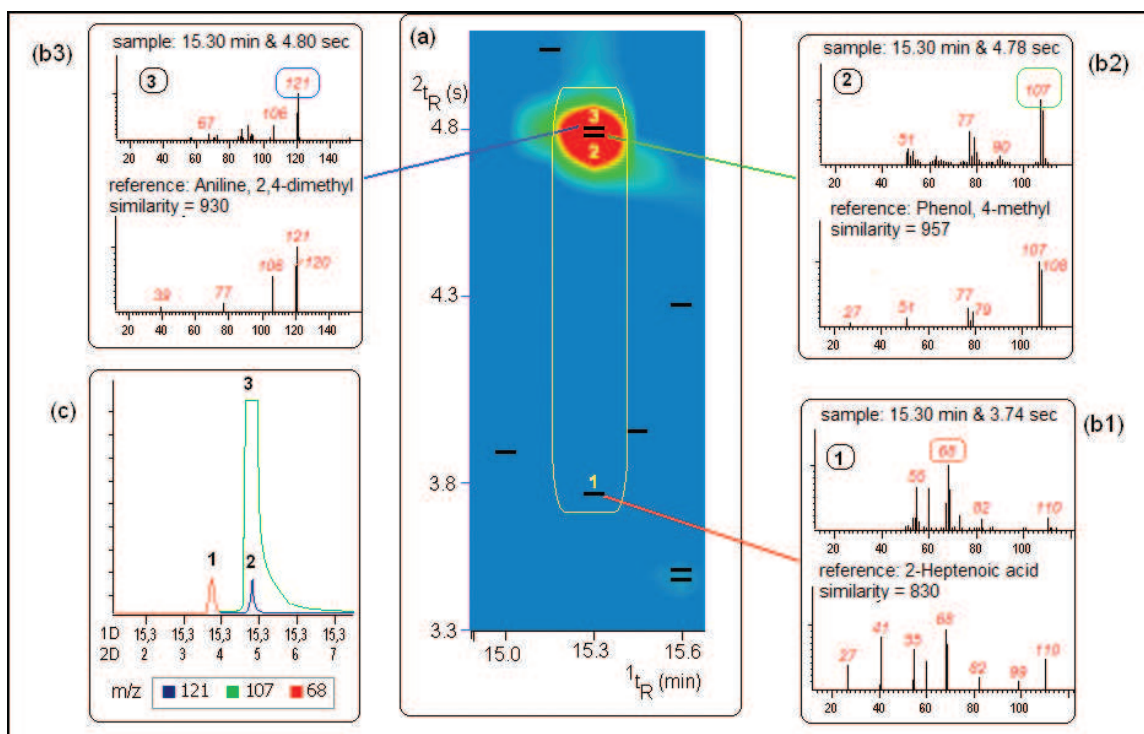


Figure 6. Peaks that co-eluted in GC/MS but were separate in GC \times GC/TOFMS. (a) Part of the 2D Diagram of the CPE bio-oil sample; (b) mass spectra of peaks 1–3 and their respective comparisons with library mass spectra; (c) reconstructed chromatogram of the peaks: peak 1 = heptenoic acid; peak 2 = C_1 phenol; and peak 3 = C_2 aniline (adapted from Onorevoli et al. [151]).

Torri et al. [136] compared the composition of bio-oils from hardwood (*Eucalyptus sp.*) and softwoods (*Picea abies*) wood residues produced in large scale in pulp and paper industries, using fast and intermediate pyrolysis. The bio-oil characterization was performed by GC/qMS and GC \times GC/TOFMS. The GC \times GC analysis allowed the detection of dimethoxy-phenols, tracing potential markers of hardwood bio-oil, which might co-elute in 1D-GC with some methoxy-phenols and benzenediols. The separation and identification of toxic aromatic polycyclic hydrocarbons by GC \times GC/TOFMS, which may also co-elute in 1D-GC with other bio-oil components, have raised the possibility of erroneous identification/quantification of these toxic components by 1D-GC due to the environmental and health risks they pose.

Tessarolo et al. [153] used GC/MS and GC \times GC/TOFMS for the chemical characterization of bio-oils from palm fruit bunch and pine wood chips prepared via flash pyrolysis. Compounds such as furanones, benzenediols, phenols, indanones, cyclopentenones, and alkylpyridines were identified. Analyses with GC/MS resulted in the detection of 166 and 129 compounds in bio-oils of empty palm fruit bunch and pine wood chips, respectively. However, GC \times GC/TOFMS allowed the detection of 631 and 857 analytes, respectively. Here, also, the superior performance of GC \times GC/TOFMS was clearly demonstrated with the use of a medium polarity stationary phase in the second dimension (BPX-50) and a nonpolar column in the first dimension (DB-5). The major classes of compounds in the two bio-oil samples were furanones, ketones, cyclopentenones, benzenediols, furans, phenols, methoxy- and dimethoxy-phenols and anhydrous sugars. Different composition profiles due to the biomass sources were found;

aldehydes, esters, and pyridines were obtained from empty palm fruit bunch bio-oil, while alcohols and cyclopentanediones were found in pine wood chips bio-oil. Negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI(-)-FT-ICR MS) was also used to analyze the same bio-oils [154]. Some low-oxygen content classes not detected by ESI-FT-ICR MS were identified by GC \times GC/TOFMS (classes from O0 to O8 with a C3 to C14). The high chromatographic resolution power of GC \times GC/TOFMS with the high dynamic m/z range of ESI-FT-ICRMS allowed the identification of volatile, nonvolatile and polar compounds of bio-oils. The same research group [155] has employed GC \times GC/TOFMS, FT-ICR-MS and hydrogen nuclear magnetic resonance (^1H NMR) to characterize bio-oils from catalytic pyrolysis of pine wood and sugar cane bagasse. The bio-oils of both bio-masses presented similar composition, differing only in the proportions found in the classes of predominant compounds. The main groups of compounds identified were acids, ketones, phenols, oxygenated heterocyclics and aromatic hydrocarbons. An increase in hydrocarbons was obtained, whenever ZSM-5 (Zeolite Socony Mobil-5) was employed, as would be expected. The three analytical techniques used were of fundamental importance for an efficient chemical characterization of the bio-oils produced.

GC \times GC with a quadrupole mass spectrometric detector (qMS) was used in the research works of da Cunha et al. [156] and Schneider et al. [157]. Da Cunha et al. have performed the fractionation of sugar cane straw bio-oil, using a silica column with pressurized liquids. A hundred sixty-six compounds were tentatively identified in the polar fraction resulting from the fractionation process (acids, aldehydes, ketones, esters, phenols, ethers, alcohols, and sugar derivatives), while the nonpolar fraction provided mainly aromatic hydrocarbons, aliphatic, cyclic and olefinic compounds [156]. Schneider et al. [157] analyzed polar compounds extracted with an alkaline solution from the *lignocell* (sawdust from forest timber) bio-oil. The results obtained in the GC \times GC/qMS system allowed the characterization of 130 compounds from different chemical classes (phenols, ethers, ketones, aldehydes, acids, alcohols, and aromatic hydrocarbons). Only thirty-five compounds were tentatively identified by GC/MS, and they belonged to the following classes: phenols, aldehydes, ketones, ethers, and acids [157]. Maciel et al. [158] also studied the pyrolysis of sugarcane straw by GC \times GC/TOFMS, with a focus on the composition of the aqueous phase. Organic solvents were employed to extract the components of the aqueous phase, and the composition of the organic extracts was similar to the one found in bio-oil, except that the aqueous phase extracts were richer in phenols, such as *ortho*, *meta* and *para* cresols. The use of GC \times GC/qMS has shown high efficiency for the analyses of bio-oils, and it is an interesting choice for this type of analyses, as its cost is lower than the one of GC \times GC/TOFMS.

5. Final comments

The basic principles of 1D-GC and 2D-GC (GC-GC and GC \times GC) have been presented, and the increased resolution, sensitivity, peak capacity, mass spectral quality, and the organized distribution of compounds that are chemically similar, in the GC \times GC chromatograms, have also been highlighted. A comparison of the application of 1D-GC and GC \times GC to complex

samples such as coal tar, coal bitumen, and pyrolytic bio-oil has shown that the special characteristics of GC \times GC provide benefits, such as speciation of difficult to separate trace compounds, such as sulfur compounds in coal tar and bitumen and nitrogen-containing compounds in coal tar. The number of compounds tentatively identified in coal-derived liquids and bio-oils is higher with GC \times GC than the ones found with 1D-GC, due to higher GC \times GC peak capacity and resolution. In addition, organized distribution of structurally related compounds in the 2D-plots is of help in the process of identification of compounds. Even though 1D-GC may be an important tool for process monitoring (pyrolysis, upgrading, etc.) as it serves to evaluate chromatographic profiles and help to determine the subsequent use of produced compounds, it can also lead to misleading results due to its insufficient performance when dealing with complex samples. Sample pretreatment before GC/MS analysis is a strategy to improve analytical performance; however, it adds one-step to the analytical process, which becomes more time-consuming, laborious, and prone to contamination. Selective detectors are also alternatives to improve 1D-GC performance whenever specific compounds are target, although they do not provide a whole view of the sample composition. The before mentioned GC \times GC analytical benefits can be of especial importance, whenever trace compound analysis is performed because of environmental and/or health issues, which is the case of the presence of sulfur and nitrogen compounds in pyrolytic or extraction liquids from coal or biomass residues. Mass spectrometric detector adds information to GC \times GC analysis, especially when spectral deconvolution (TOFMS) is employed for compounds that partially co-elute and GC \times GC/qMS is a good choice for a less costly GC \times GC/MS analysis. A more comprehensive and detailed analysis of coal derived liquids and also of bio-oils is of importance, as far as these liquids are potential alternative sources of high added-value products and also as alternative fuels. The same knowledge is important for the development of environmentally safe technologies for the production of coal derived liquids and pyrolytic liquids of biomass residues, which are of interest to the chemical industry. These liquid samples are extremely complex, contain a great number of different compounds and chemical classes and are also very diverse due to the original variety of coals and residual biomasses, as well as due to the different parameters that may be employed during production and upgrading processes. This variability in terms of raw material input and process poses a great analytical challenge, which is addressed to a great extent by GC \times GC/TOFMS, without the need of previous laborious sample pretreatment, or multiple chromatographic steps, while keeping analysis time in the range of a 1D-GC analysis. However, as bio-oils and coal derived liquids are extremely complex samples, other instrumental techniques should also be employed along with GC \times GC/TOFMS to achieve a total characterization of these samples, such as liquid chromatography with mass spectrometric detector, infrared spectroscopy, among others.

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