

Full Length Article

Rapid hydrocarbon group-type semi-quantification in crude oils by comprehensive two-dimensional gas chromatography

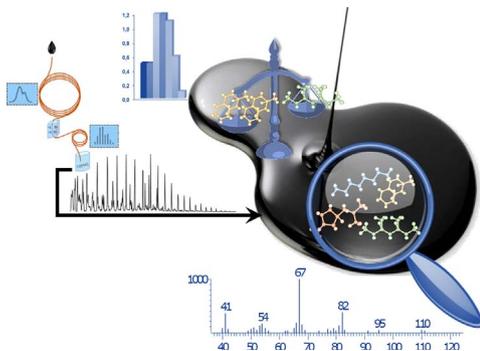
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GRAPHICAL ABSTRACT



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ABSTRACT

Petroleum is the main source of energy used in the world. The oil industry faces challenges in trying to understand the chemical composition of crude oils, quantitatively and qualitatively. The application of specific and sophisticated techniques allows a detailed characterization and provides important information that impacts from the exploration to production, transportation, and crude oil refining. A set of twelve crude oil samples with different API gravity were analyzed via comprehensive two-dimensional (2D) gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) aimed at the detection, identification and semi-quantification of hydrocarbon classes using extracted ion chromatogram (EIC) and total ion chromatogram (TIC). The use of the polar/non-polar column configuration provided better separation between the hydrocarbon classes which allowed the identification and semi-quantification of the same. Therefore, series of *n*- and *iso*-alkanes, alkyl-cyclohexanes, alkyl-cyclopentanes, alkyl-decalines, alkyl-naphthalenes, alkyl-phenanthrenes and alkyl-9H-fluorenes were characterized. In the present study, a semi-quantification approach to data assessment using TIC is proposed. Comprehensive evaluation provided the chromatographic fingerprint of each sample in a single analysis followed by the semi-quantification of the hydrocarbon classes. The oil samples presented completely different hydrocarbon class data, even when presenting similar API gravity values. Branched alkanes and *n*-alkanes were the major semi-quantified compounds, and branched alkane concentrations were higher than *n*-alkanes in the majority of samples. These results afford valuable information for the petrochemical industry.

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GC × GC-TOFMS was applied for speciation and group-type semi-quantification using a single oil drop without a fractionation or clean up step.

1. Introduction

The compositional analysis of petroleum via separation of classes provides valuable information to understand the behavior between different types of crude oils. Petroleum can be qualitatively and quantitatively characterized by various separation techniques. Group-type separation is an essential, traditional approach used to separate and classify crude oil, based on oil components' solubility, which involves separation into saturate hydrocarbon (saturates), aromatic hydrocarbon (aromatics), resins, and asphaltenes (SARA) fractions [1–3]. Although a large number of procedures for SARA separation have been developed and applied for decades, including gravimetric adsorption chromatography, an American Society for Testing and Materials standard test method [4,5], most shows inadequacies, such as extensive cross-contamination, poor analytical precision [6], diversity of the methods and lack of uniformity. High performance liquid chromatography (HPLC) has been applied in petroleum products and samples [7–10]. However, this technique presents limitations, such as the difficulty of quantifying isolated fractions [11]. In addition, thin-layer chromatography with flame ionization detection (Iatroscan TLC-FID) is a fast method for SARA analysis applied in petrochemical industries. This instrument offers accurate method for quantifying SARA fractions in solvent extracts [12]. However, Iatroscan TLC-FID provides only the amount of the four major classes, not a group type characterization.

Recently, Bissada et al. [6,13] reported a novel automated multi-dimensional high performance liquid chromatography (AMD-HPLC) for SARA separation and quantification. The AMD-HPLC system is fully automated and uses a set of two columns; it is based on a combination of adsorption and partition chromatography and separates SARA fractions and *n*-paraffins, *iso*-paraffins and naphthenic (PIN) fractions. Although the system shows good performance, further attention should be paid to the use of other chromatographic techniques to evaluate the purity of the fractions obtained by this method. Another technique that has become widely used to characterize polar compounds in crude oils and petroleum fractions is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [14–16]. The ultrahigh resolution and mass accuracy allows the assignment of the elemental composition and classification considering the number of heteroatoms of oxygen, nitrogen and others [17].

On the other hand, Vendevre et al. [18] previously noted that group-type separation by comprehensive 2D gas chromatography (GC × GC) provides detailed information about samples when compared to other methods. In numerous previous studies, GC × GC has been reported in the quantitative analysis of environments [19,20], foods [21], petrochemicals [22–26], cosmetics [27] and bio-oils [28,29]. However, most studies use GC × GC with flame ionization detector (FID) for quantitative analysis. The combination of GC × GC and time-of-flight mass spectrometry (TOFMS) has been much employed in qualitative analysis and offers a detailed characterization about the chemical composition of complex mixtures, such as petroleum, but the quantitative approach is still much less commonly used in complex matrices [30,31]. In complex matrices such as petroleum, coelutions still can occur, thus the coupling of the TOFMS as the detection system can be considered a third dimension, providing a reliable identification through the mass spectrum and an additional separation capacity by the spectral deconvolution algorithm. The deconvolution procedure consists of a data treatment used for the mathematical

separation of coeluted peaks chromatographically showing minor differences in retention time in the Gaussian distribution of the ions within the signal for the total ions. Thus, it is possible to discriminate and obtain the mass spectra of the substances [32]. The spectral deconvolution process allows the choice of a selective ion for the EIC, where through this it is possible to obtain area information and retention time of substances classes that elute in the same region in the chromatographic plane. There is why TOFMS is so important in complex samples analyses because even with two dimensions there are classes superpositions in the chromatogram.

Quantitative analysis using GC × GC-TOFMS is more complex than one-dimensional gas chromatography (1D-GC). Due to the modulation process, a single peak is sliced into several small peaks, and its quantification requires the integration of each of these peaks to obtain the total area of the target compound [33]. Additionally, despite the high peak capacity, coelution between interferers and the target compound may occur [34], therefore, it is necessary to verify the mass spectra of each slice. Ávila et al. [35] presented a group-type separation and identification of several individual compounds and a quantitative analysis after data processing using GC × GC-TOFMS. This study was performed on extra heavy gas oil (EHGO) samples obtained by molecular distillation. Series of aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons and sulfur compounds, were quantified. Further, triaromatic steroids, methyl-triaromatic steroids, tetrahydrochrysenes and tetraaromatic pentacyclic compounds were present in EHGO samples. Jennerwein et al. [31] showed the combination of mass spectral data and retention times in both dimensions within the automated scripts. This approach provides not only the details of the 2D chromatogram, but also avoids false classifications. Most recently, Silva et al. [29] applied GC × GC-TOFMS for the individual quantification of products in bio-oil samples obtained from three different processes: real thermal, catalytic and hydrodeoxygenated bio-oil. Quantification was performed with reliability using the analytical curves of oxygenated standards, hydrocarbons and deuterated internal standards. Also, in the study, a semi-quantification by classification was performed as a preliminary evaluation regarding the composition of the samples.

The characterization of organic compounds in oil samples is difficult to accomplish due to variety of chemical classes, each with different characteristics of volatility, polarity, and concentration. Currently, the petroleum industry has a great interest in connecting the effect of hydrocarbon class concentrations with the different properties of crude oils, as the traditional physical-chemical parameters alone are insufficient to understand petroleum behavior and application in transport and refining. The available analytical tools do not allow to know its composition completely because to the complexity of petroleum samples. The use of GC × GC-TOFMS has been considered valuable, especially in relation to the generated image because, with this technique, it is possible to obtain the structured chromatogram that distinguishes compounds of the same class, which interact differently in the second column, in specific chromatographic regions.

Thus, the present study aims the qualitative and semi-quantitative chemical composition characterization of individual compounds and main hydrocarbon classes in twelve Brazilian crude oils with different API gravities. Additionally, GC × GC-TOFMS was also applied in a single chromatographic analysis without a fractionation step to obtain the total area of the main hydrocarbon classes.

Table 1
General properties of crude oil samples in this study.

Sample	Density (°API)	Pour Point (máx/min) (°C)	Viscosity 30 °C (mm ² /s) [*]	Viscosity 40 °C (mm ² /s) [*]
B01	27.0	−6	31.17	20.88
B02	30.0	12	17.44	12.2
B03	27.4	< −24	−	−
B04	31.0	6	18.18	12.83
B05	17.3	−6	1084	489.6
B06	14.8	3	−	−
B07	36.0	36	14.39 (at 50 °C) ^{**}	9.829 (at 60 °C) ^{**}
B08	28.9	−15	23.53	16.7
B09	32.3	12/−27	14.95	10.26
B10	23.7	21/0	218.0	110.0
B11	44.5	9 / 6	2.032	1.727
B12	17.7	21 / 6	2637	944.3

^{*} Reference data.

^{**} Different temperature for paraffinic oil.

2. Material and methods

2.1. Samples

Twelve samples were selected based on their °API difference (14.8–44.5). The crude oil samples and selected physical properties, which were supplied by Petrobras R&D Centre, are listed in Table 1. These samples were submitted to GC-FID analysis, getting the whole oil fingerprints and their chromatograms are shown in Fig. 1S (Fig. 1S and GC-FID conditions, supplementary material).

Approximately 10 mg of each sample were weighed directly in a vial, followed by the addition of deuterated internal standards solution at 10.0 µg mL^{−1} and were dissolved in dichloromethane (Tedia, Brazil) for semi-quantification via EIC and TIC using GC × GC-TOFMS. The internal standards used for semi-quantification were acquired from CDN Isotopes (Quebec, Canada) and have a purity greater than 97%: *n*-hexadecane-D₃₄, *n*-tetracosane-D₅₀, pristane-D₄₀, pyrene-D₁₀, dibenzothiophene-D₈ and cholestane-D₆.

The crude oil samples (ca. 100 mg) were also fractionated into saturated, aromatic and polar compounds by liquid chromatography, using

activated silica gel (3.0 g, 120 °C/12 h; 0.063–0.200 mm, Merck, Darmstadt, Germany) and the fractions were quantified using gravimetric method. Approximately 100.0 mg of each oil was weighed on analytical balance and dissolved in 1 mL of *n*-hexane. This mixture was added to the top of the column previously filled with silica gel. The saturated fractions were eluted with 10 mL of *n*-hexane, aromatic fractions with 10 mL of *n*-hexane/dichloromethane solution (8:2), and polar fraction was eluted with 10 mL dichloromethane/methanol solution (9:1). The fractions were collected in 50 mL flasks and the solvent was removed on a rotary evaporator [36,37].

2.2. GC × GC-TOFMS

The GC × GC-TOFMS system used was a Pegasus 4D (Leco Corporation, St. Joseph, MI, USA), which is an Agilent Technologies 7890 GC (Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet dual-stage modulator. Data acquisition and processing were carried out using ChromaTOF™ version 4.51 software (Leco Corporation, St. Joseph, MI, USA). The GC column set consisted of a DB-17 (Agilent Technologies), 50%-phenyl-50%-dimethyl-siloxane (30 m, 0.25 mm i.d., 0.25 µm d_f) as the first dimension (¹D) and a DB-5 (Agilent Technologies), 5%-phenyl-95%-dimethyl-siloxane (1.2 m, 0.18 mm i.d., 0.18 µm d_f) as the second dimension (²D). The second column was connected to the TOFMS by an uncoated deactivated capillary (0.5 m × 0.25 mm i.d.). The columns and the uncoated deactivated capillary were connected by SGE unions using SilTite™ metal ferrules (Ringwood, VIC, Australia) for 0.10–0.25 mm i.d. GC columns.

The injection conditions were performed in splitless injection mode of 0.5 µL at 310 °C and a purge flow of 6 mL min^{−1}. The primary oven temperature program was 40 °C for 5 min, ramped at 3 °C min^{−1} to 330 °C, and the secondary oven temperature program had a temperature 5 °C higher than that of the primary oven. Helium was used as the carrier gas at a flow rate of 1 mL min^{−1}. The modulation period was 9 s with 2.25 s hot pulse duration and a 15 °C modulator temperature offset versus the secondary oven temperature. The mass spectrometer transfer line was held at 280 °C, and the TOFMS was operated in 70 eV electron ionization mode with a collected mass range of 40–650 Da. The ion source temperature was maintained at 230 °C, the detector was operated at −1394 V, and the acquisition rate was 100 spectra s^{−1} [14].

In order to obtain a better separation of the saturated hydrocarbons

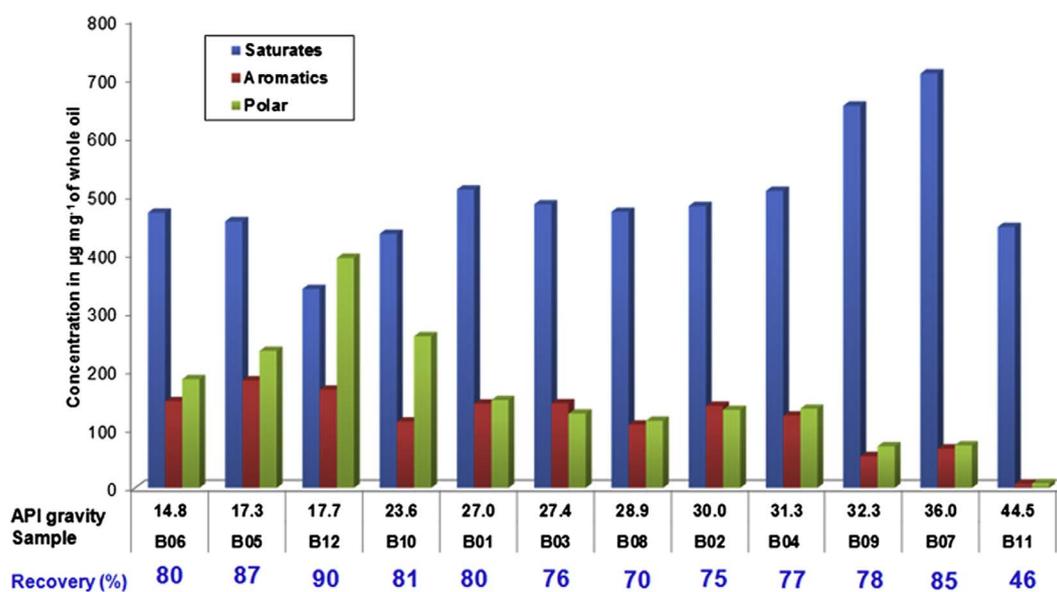


Fig. 1. Distribution of SAP fractions in crude oil samples obtained from LC and gravimetry, arranged in order of °API.

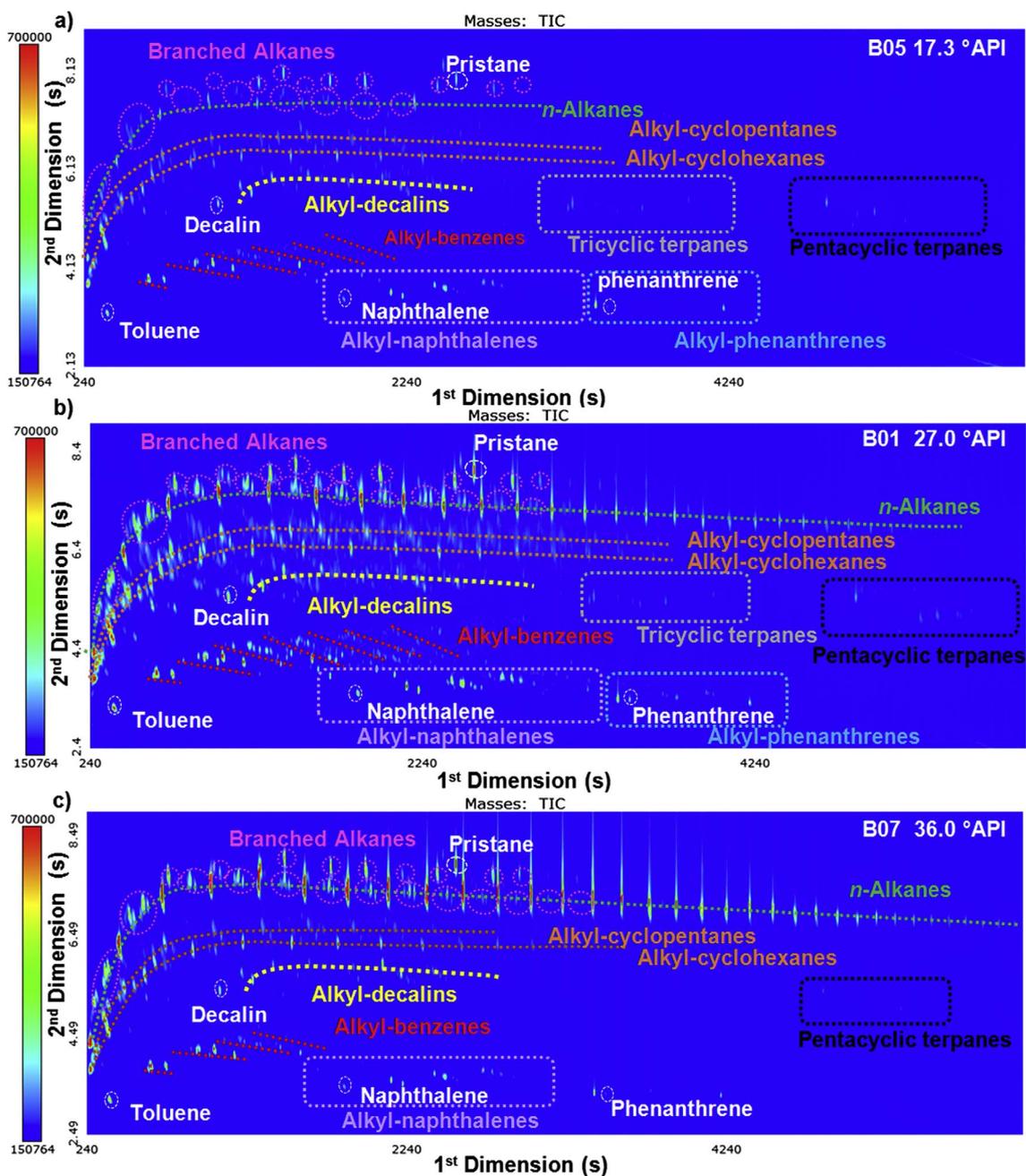


Fig. 2. GC \times GC–TOFMS TIC of crude oil samples B05, B01 and B07, illustrating hydrocarbon class distribution.

in chromatographic plane, different conditions were tested and presented in Vanini et al. [14]. The polar/non-polar column set provided better separation between the hydrocarbon classes, which allowed their identification and semi-quantification [14].

Compound identification was performed by examination and comparison to literature mass spectra, retention time, elution order [18,35,38–40], authentic standards, and National Institute of Standards and Technology (NIST) Mass Spectral Database (version 2.0).

2.3. Semi-quantitative analysis

GC \times GC-TOFMS data acquisition and processing were performed using ChromaTOF® software version 4.51 (Leco, St. Joseph, MI, USA). After data acquisition, samples were subjected to a data processing

method in which individual peaks were automatically detected based on a 50:1 signal-to-noise ratio.

The semi-quantitative evaluation of identified classes was achieved using a different approach: semi-quantification by total ion chromatogram (SQTIC). The class semi-quantification was performed using the sum of all peak areas from each class in relation to the peak area of the internal standard at known concentration. For each class, a specific internal standard was applied, e.g., *n*-hexadecane-D₃₄ for the saturated hydrocarbon classes up to 20 carbon atoms and pyrene-D₁₀ for the aromatic hydrocarbons classes. Later, this concentration was corrected to the initial crude oil mass ($\mu\text{g g}^{-1}$).

SQTIC is another mode of data treatment which uses the ChromaTOF® software to consider general classes. For this semi-quantification mode, classifications were created for each sample based on

the delimitation of regions for the main hydrocarbon classes, and TIC was used to obtain the total area. It is important to note that the classes are divided into *n*-alkanes, branched alkanes, monocyclic, bicyclic and polycyclic hydrocarbons, alkyl-benzenes, alkyl-naphthalenes, alkyl-phenanthrenes and alkyl-9H-fluorenes.

The class concentration was corrected to the initial crude oil mass (in milligrams) using the formula: (obtained class area/internal standard area) \times (standard mass in nanograms/crude oil mass in milligrams), where standard mass is the standard concentration (nanograms/microliter) \times standard volume (in microliters).

3. Results and discussion

3.1. LC analysis

The crude oil samples were fractionated by liquid chromatography (LC) in order to provide preliminary information about saturated hydrocarbons, aromatic and polar compounds (SAP) fractions. The LC results with the SAP fractions are shown in Fig. 1 along with the recovery data, where the major contents were between 70% and 90%, with the exception of 46% for sample B11. These recoveries can be explained by the loss of volatile compounds, as well as the adsorption of polar ones on silica beds [6,13] (in sample B11, the low recovery may be due to the fact that it is a condensate, i.e., a fluid quite rich in low boiling point hydrocarbons).

According to the density ($^{\circ}$ API) values, samples are classified in heavy oils (B05, B06, B12), intermediate oils (B10, B01, B03, B08, B02) and light oils (B04, B07, B09, B11). However, results from LC analysis show that sample B10 (intermediate oil) has a SAP composition similar

to a heavy crude oils; similarly, sample B04 (light oil) presented fraction concentrations similar to an intermediate crude oil samples.

Although samples B06 and B05 have different $^{\circ}$ API values (14.8 and 17.3, respectively), both present similar compositions in relation to the class concentration. The same is observed between samples B09 and B07. Despite this type of characterization gives preliminary information about the crude oil samples, it is not sufficient to understand their physicochemical properties; that requires a more detailed characterization.

3.2. Qualitative analysis via GC \times GC-TOFMS

The GC \times GC-TOFMS qualitative analyses are shown in Fig. 2 and the hydrocarbon classes in the studied crude oil samples were classified as alkanes, cycloalkanes also called naphthenic (alkyl-cyclopentanes, alkyl-cyclohexanes, alkyl-decalines), monocyclic aromatic hydrocarbons (alkyl-benzenes), polycyclic aromatic hydrocarbons (alkyl-naphthalenes, alkyl-9H-fluorenes, alkyl-phenanthrenes), and other series. The structural organization in 2D separation space also allows visualization of classes according to the physicochemical properties of their components [41].

Fig. 2 illustrates the chromatographic fingerprint of three representative samples from the set of twelve crude oils selected according to $^{\circ}$ API (B05-heavy, B01-intermediate, B07-light). Most of the samples present an extensive range of carbon atoms for *n*-alkanes (C8–C41), except for samples B05, B06 and B11. Sample B11 presents a smaller range since it is a light oil. The sample B05 is a heavy oil containing a low concentration of *n*-alkanes; consequently, it presents smaller range. For sample B06, *n*-alkanes were not detected in this

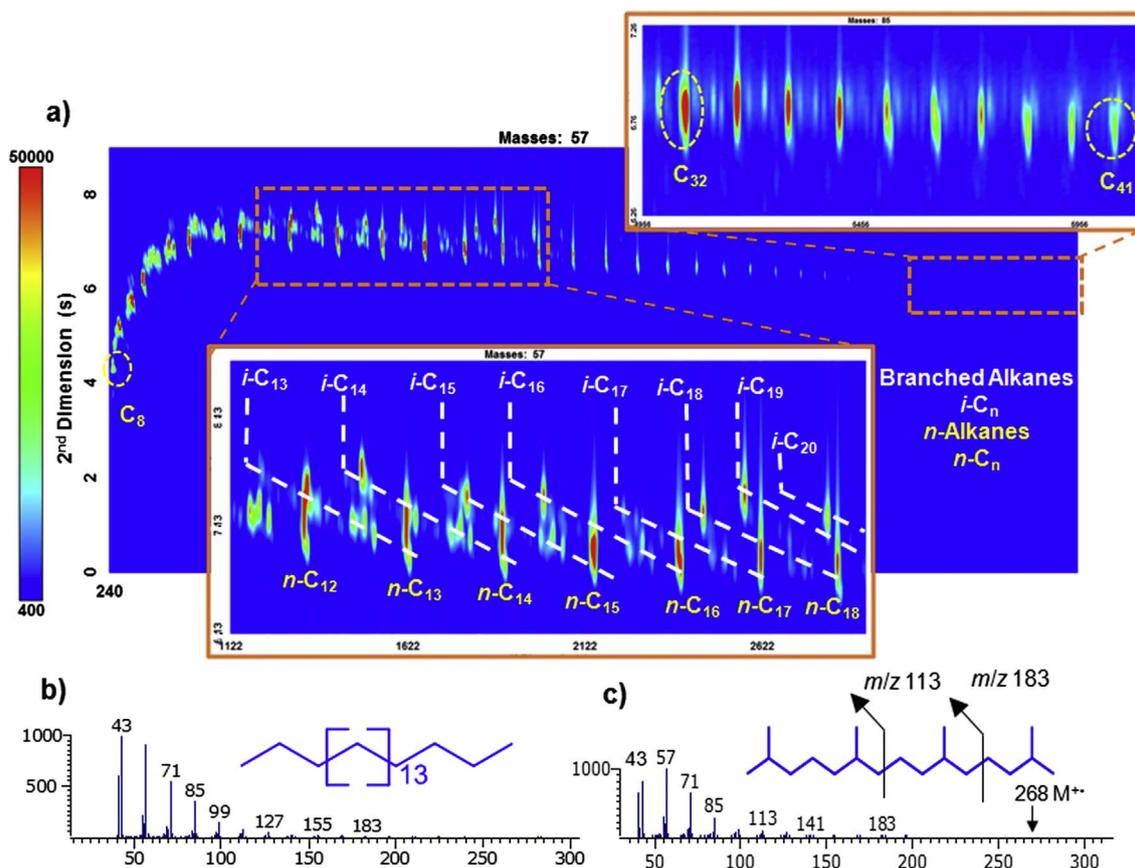


Fig. 3. (a) GC \times GC-TOFMS chromatograms highlighting the branched alkanes and *n*-alkanes identified in all samples. Mass spectra of: (b) eicosane and (c) 2,6,10,14-tetramethylpentadecane (pristane).

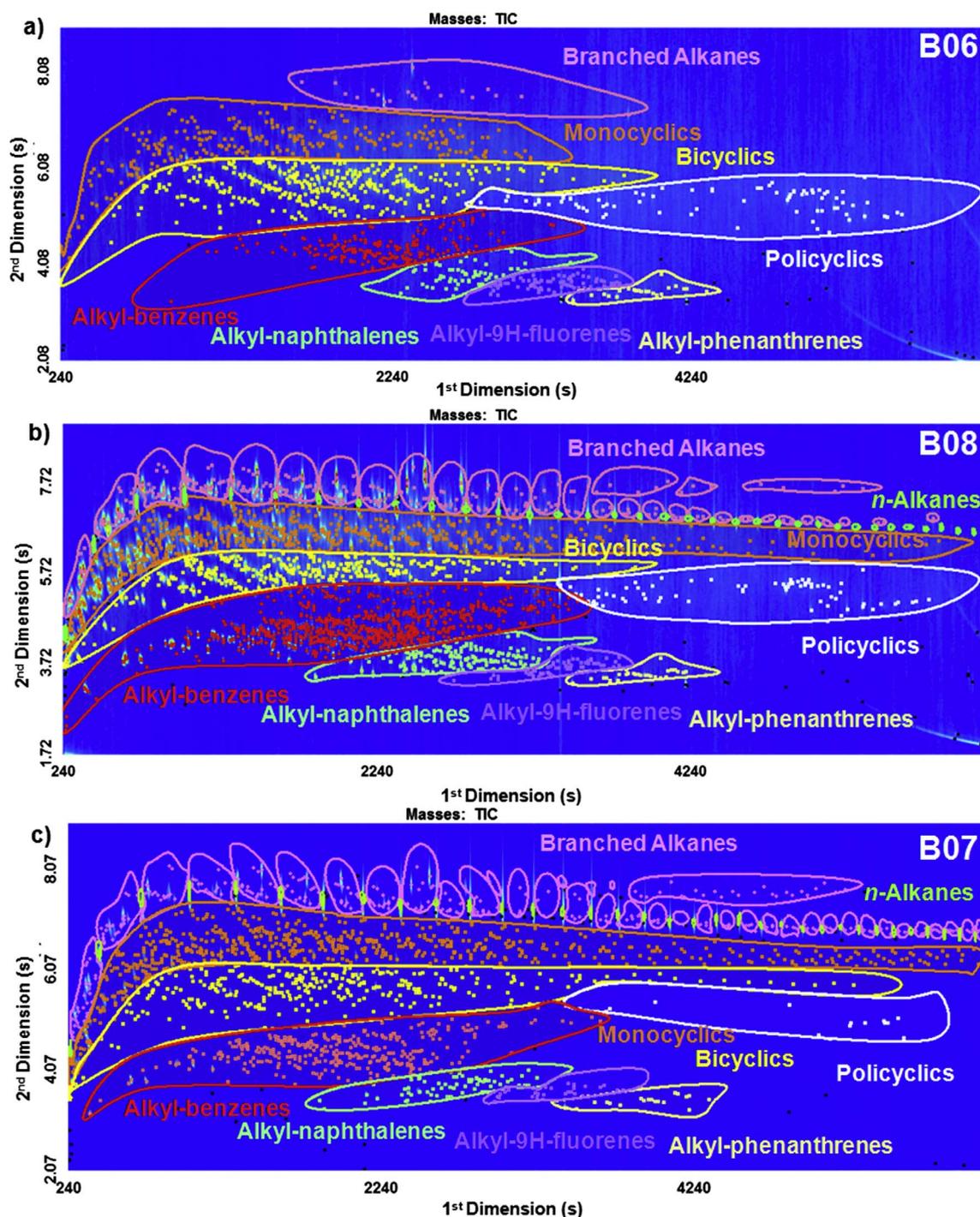


Fig. 4. TIC of samples B06, B08, and B11, illustrating classifications in the two-dimensional space obtained by the SQTIC method.

range of carbon atoms, also due to their low °API. Moreover, Fig. 3 illustrates the efficient separation between identified main hydrocarbon classes, such as *n*-alkanes and branched alkanes. The branched alkanes elute between the *n*-alkanes, thanks to some polarity induced by the increase of branching in the paraffinic main chain which is nearly impossible when using conventional GC [42]. The major and most abundant monocyclic compounds were identified as alkyl-cyclopentanes, alkyl-cyclohexanes and alkyl-methylcyclohexanes from their *m/z* 69, 83 and 97 ions, respectively (Fig. 2S, supplementary material). Fig. 3S (supplementary material) shows bicyclic hydrocarbons that were identified in samples.

Alkyl-naphthalenes, alkyl-phenanthrenes and alkyl-9H-fluorenes were also detected in all samples (Fig. 4S, supplementary material), at low intensity when compared to saturated hydrocarbons. Furthermore, pyrene was only identified in samples B05, B01 and B02. It is possible to note that the increase of the aromatic ring number led to a reduction in retention time of substances in 2D, while the increase in the number of the carbon atoms increased the retention time in 2D [38]. These aromatic compounds are arranged by roof-tile effect [42], where the orientation of the tiles starts in the upper left and goes to the lower right. In other words, a low volatility and high solubility in polar column (1D) allow the effect to occur [18].

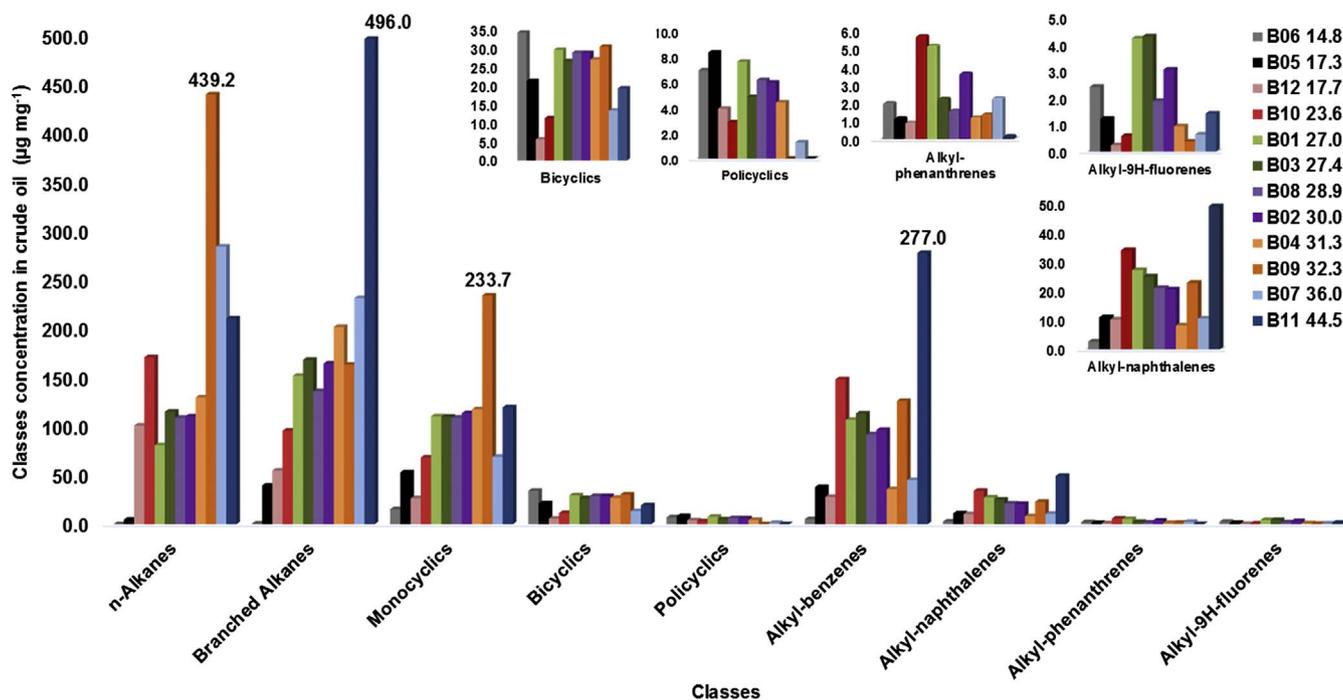


Fig. 5. Concentration ($\mu\text{g mg}^{-1}$) of hydrocarbon classes in whole oil samples analyzed by GC \times GC-TOFMS using SQTIC.

Table 2

Concentration of hydrocarbon classes ($\mu\text{g mg}^{-1}$) semi-quantified in crude oil samples using SQTIC.

Class	Samples/ $^{\circ}$ API											
	B06	B05	B12	B10	B01	B03	B08	B02	B04	B09	B07	B11
	14.8	17.3	17.7	23.6	27.0	27.4	28.9	30.0	31.0	32.3	36.0	44.5
n-Alkanes	n.d.	4.6	100.6	170.5	80.7	114.9	108.6	110.1	129.4	439.2	283.6	210.3
Branched Alkanes	0.5	39.5	54.7	95.4	151.6	167.9	135.9	164.0	201.5	163.0	231.0	496.0
Monocyclics	15.3	52.8	26.5	68.1	110.2	109.7	108.8	113.3	117.4	233.7	68.8	119.4
Bicyclics	34.1	21.2	5.6	11.5	29.5	26.5	28.7	28.7	26.9	30.3	13.3	19.2
Polycyclics	6.9	8.3	3.9	2.8	7.6	4.8	6.2	6.0	4.4	n.d.	1.3	n.d.
Saturates	56.8	126.4	191.3	348.1	379.6	423.8	388.2	422.1	479.6	866.2	598.0	844.8
Alkyl-benzenes	5.0	38.0	27.8	148.0	106.6	113.0	91.7	96.2	35.8	125.9	45.0	277.0
Alkyl-naphthalenes	2.6	11.0	10.2	34.1	27.3	25.1	21.1	20.6	8.2	22.9	10.6	49.2
Alkyl-phenanthrenes	2.0	1.2	0.9	5.7	5.2	2.2	1.6	3.7	1.2	1.4	2.3	0.2
Alkyl-9H-fluorenes	2.4	1.2	0.2	0.6	4.2	4.3	1.9	3.1	0.9	0.4	0.6	1.4
Aromatics	12.0	51.4	39.1	188.4	143.3	144.6	116.3	123.6	46.1	150.6	58.5	327.8
Sum	68.8	177.8	230.4	536.4	522.9	568.4	504.4	545.6	525.8	1016.6	656.4	1172.7

n.d.: not detected.

3.3. Semi-quantitative analysis via GC \times GC-TOFMS

SQTIC is a different mode of data acquisition, which is poorly reported in the literature [26,31] and the class type separation has become advantageous in view of the complexity of the samples such as petroleum [43]. In this method, classifications are made for each sample based on the delimitation of the regions for the main hydrocarbon classes, and TIC is used to obtain the total area. In summary, Fig. 4 represents a typical two-dimensional chromatogram with classifications, where each peak marker is a substance and the different classes are indicated with different colors. ChromaTOF™ integrates the total area of each class from TIC. An important feature is the rapid hydrocarbon group-type semi-quantification and the possibility of applying the classification from a sample to others that contain similar fingerprint by making only a few adjustments.

The distribution of the concentrations obtained via SQTIC for the hydrocarbon classes identified in samples are presented in Fig. 5 and Table 2. It is evident from the graphic distribution presented in Fig. 5 that all samples had higher concentrations of branched alkanes than n-alkanes, except for samples B07 and B12.

According to the LC method, samples B05 and B06 showed a very similar concentration of the fractions, mainly for saturated ones ($B05 = 455.2 \mu\text{g mg}^{-1}$; $B06 = 470.0 \mu\text{g mg}^{-1}$), even though both present differences greater than 1° API. However, through detailed semi-quantification using SQTIC, note that these samples presented different concentration values of specific classes from saturated hydrocarbons; for example, sample B05 has $0.5 \mu\text{g mg}^{-1}$ of branched alkanes, while sample B06 had $39.5 \mu\text{g mg}^{-1}$. This difference also existed between samples B01 and B04 which showed concentration values similar to saturates ($B01 = 509.5 \mu\text{g mg}^{-1}$; $B04 = 507.3 \mu\text{g mg}^{-1}$) and aromatics

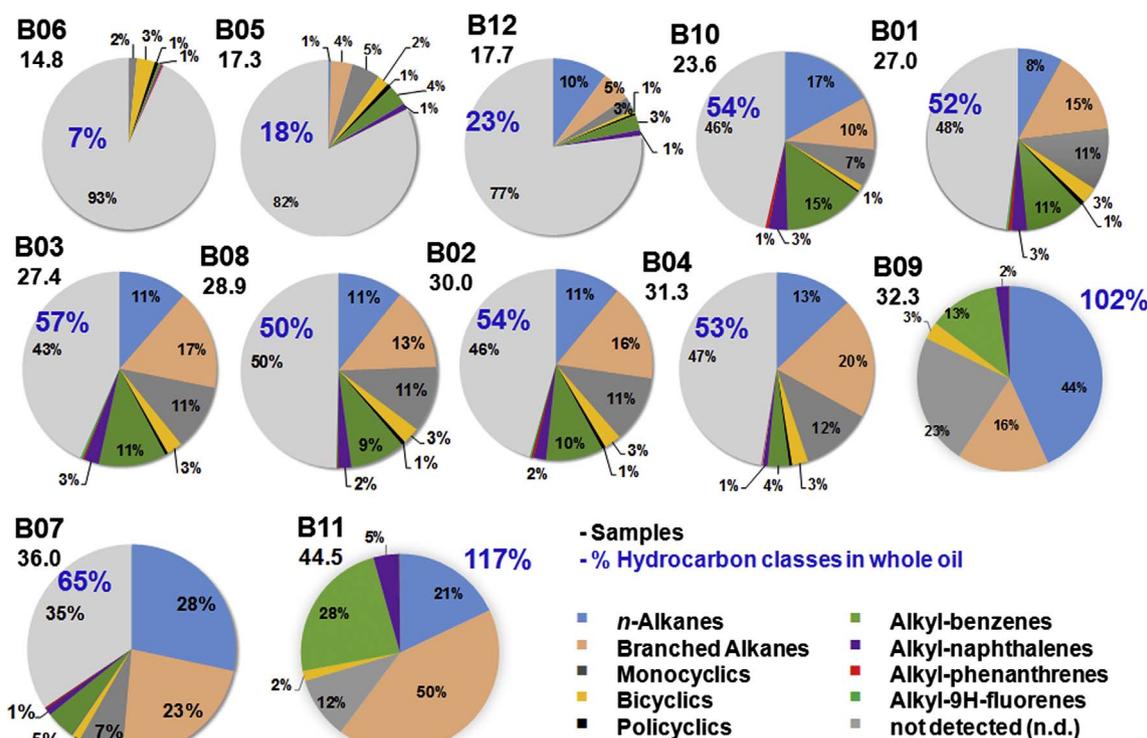


Fig. 6. Percentage (%) of hydrocarbon classes in whole oil samples obtained by the SQTIC method.

(B01 = 113.2 $\mu\text{g mg}^{-1}$; B04 = 123.4 $\mu\text{g mg}^{-1}$) fractions, while the results from SQTIC showed differences mainly in the branched alkanes, alkyl-benzenes, and alkyl-naphthalenes. The same behavior occurred for sample B07 compared to sample B09. In contrast, samples B05 and B12 had small differences in their $^{\circ}\text{API}$ values (B05 = 17.3; B12 = 17.7) and different saturated fraction concentration (B05 = 455.2 $\mu\text{g mg}^{-1}$; B12 = 339.0 $\mu\text{g mg}^{-1}$). Meanwhile, the SQTIC method showed a considerable difference in *n*-alkane class concentrations (B05 = 4.6 $\mu\text{g mg}^{-1}$; B12 = 100.6 $\mu\text{g mg}^{-1}$). Thus, the observed differences between the $^{\circ}\text{API}$ values for these samples may be explained by the concentration of the more specific classes. In this way, the detailed group-type characterization provides specific data and observations of the oils, as samples with small $^{\circ}\text{API}$ differences can present different profiles of class concentration and, consequently, differences in their physico-chemical properties, as seen in Table 1. As an example, sample B12 presented ca. twice the viscosity of the sample B05. The combination of these results with the physico-chemical properties offers valuable information for the petroleum industry, allowing for a better oil refining plan and for obtaining products with higher added value.

In addition, Fig. 6 shows the amount of each hydrocarbon class that was semi-quantified via SQTIC, as well as the total hydrocarbons in crude oil samples and the amount that was not detected, identified, and semi-quantified by the SQTIC method. Note that samples with intermediate $^{\circ}\text{API}$ (B10, B01, B03, B08, B02) and light oil samples (B04, B07), present about 50–65% of the hydrocarbon classes. Results indicated that light oil sample B04 had a concentration profile similar that of an intermediate oil. It is necessary to emphasize that it was possible to semi-quantify, respectively, 102% and 117% of the hydrocarbon classes in samples B09 and B11, and, although these exceeded 100%, both values were acceptable (< 120%).

These results not only allow graph construction that is useful to compare the class proportions in crude oil samples (Fig. 6), but also

allow visualization of the major components in each class using the two-dimensional bubble-plot chromatogram (Fig. 7). Furthermore, it is possible to perform a detailed mapping of the most abundant components of each class in a sample from the same analysis.

Oils with intermediate $^{\circ}\text{API}$ values show comparable results, reaching similar values (Fig. 5S and Fig. 6S, supplementary material). Saturated and aromatic hydrocarbon concentrations for intermediate crude oil presented comparable values. However, for heavier and lighter oils, different results were observed as a function of different technique discrimination. For heavy oils, results obtained by SAP are higher than SQTIC because non-volatilizable compounds cannot be detected due to gas chromatographic conditions. Meanwhile, saturated and aromatic hydrocarbon concentrations for light oils obtained using SQTIC are higher than concentration values obtained SAP fractions, due to the problems related to the loss of volatile compounds by evaporation. Furthermore, the data obtained by GC \times GC-TOFMS (SQTIC) provide more detailed class information than the obtained by the LC method (SAP). This allows to understand the different behaviors between crude oils presenting small $^{\circ}\text{API}$ differences.

Finally, results presented in this work are far more detailed and precise than those provided by more classical techniques, such as oil fractionation, which have failed to discriminate among the different profiles of samples with similar $^{\circ}\text{API}$ values.

4. Conclusion

This study developed, optimized, and applied a group-type semi-quantification in Brazilian crude oils of different values of $^{\circ}\text{API}$, using a single oil drop without any fractionation or clean up steps using GC \times GC-TOFMS. Through SQTIC, it carried out a more detailed investigation of the petroleum samples to understand the differences in their behavior in a wide range of API gravities. Oils were differentiated

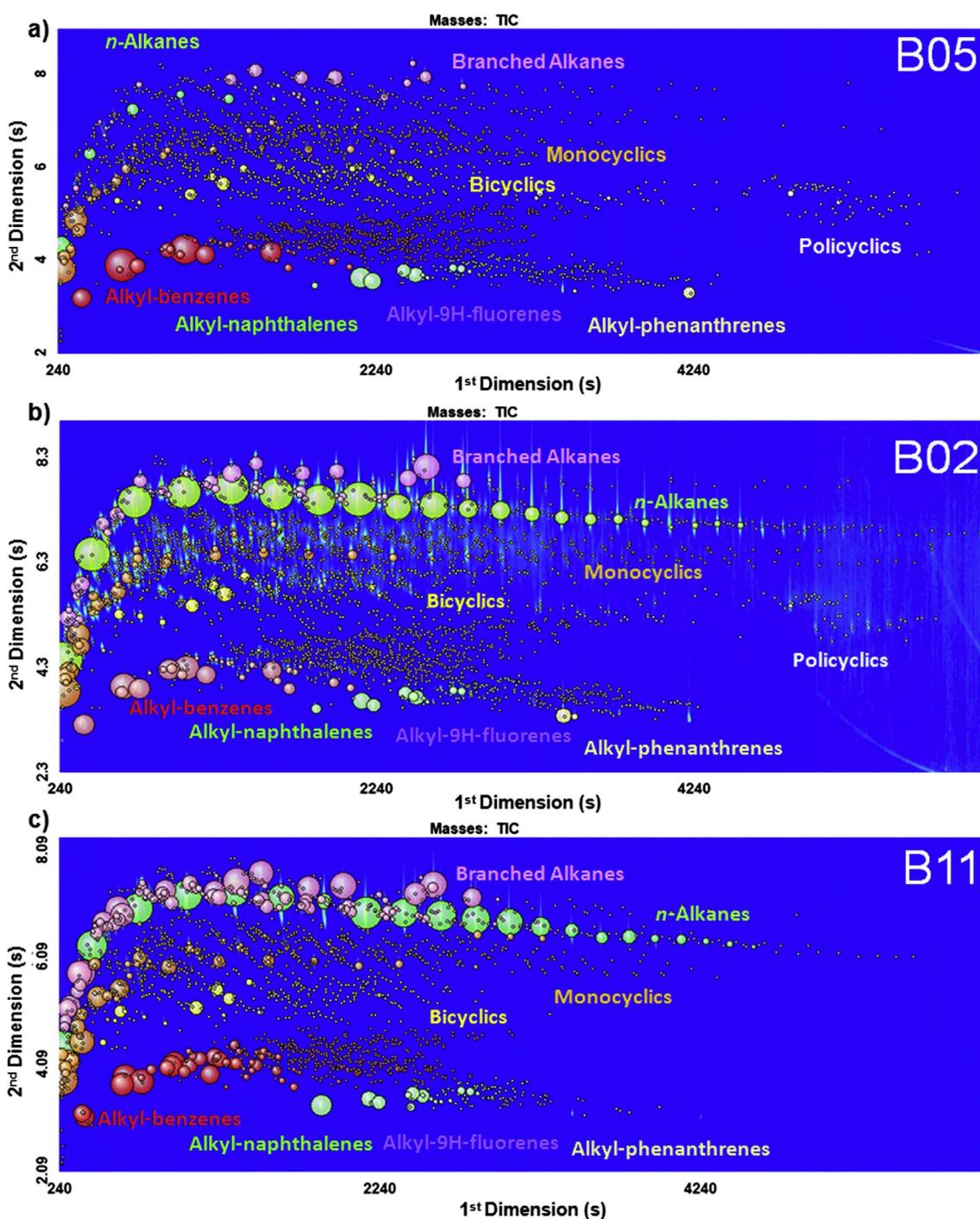


Fig. 7. Bubble chromatogram from classification selection for the data analysis that represents the relative abundance of hydrocarbon classes for samples B05, B02, and B11.

qualitatively, mainly semi-quantitatively, even when presenting similar API gravities. Branched alkanes and *n*-alkanes were the major classes quantified, and presented distinct values, with the branched alkanes predominant in most samples.

Finally, this work allowed the development of a rapid assessment method that provides detailed information about crude oils and their properties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2018.02.009>.

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